A HALF-CENTURY OF CHEMISTRY IN AMERICA
1876–1926

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HISTORICAL REVIEW COMMEMORATING
THE FIFTIETH ANNIVERSARY OF THE
AMERICAN CHEMICAL SOCIETY

EDITED BY

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Chairman, Committee for the Historical Program
of the Semicentennial Meeting

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INTRODUCTION

The present volume, with its story of the efforts to establish a national organization of chemists and with its reviews of progress in various branches of chemistry, is the response to a general desire to commemorate in some suitable way the Fiftieth Anniversary of the American Chemical Society.

The annals of American chemistry contain the accounts of organizations, meetings, publications, and reviews of progress previous to the establishment of the American Chemical Society in 1876. The Chemical Society of Philadelphia, the first chemical society in the world, was founded in 1792, and, during its existence of some seventeen years, published various annual orations that were delivered before its members. This organization was succeeded in 1811 by the Columbian Chemical Society of Philadelphia, which is said to have edited two volumes of "Memoirs," although only the first of these, published in 1813, has thus far come to light. The articles in that volume upon theoretical, mineralogical, physiological, analytical, and other branches of chemistry are the first collected evidences of chemical research in America. The membership of the Columbian Chemical Society was scattered through several different states and, although its existence was cut short by the troubled conditions which accompanied the War of 1812, the organization is notable as representing the first attempt to establish in America a national association of chemists with a distinctively chemical publication.

Following the dissolution of the Columbian Chemical Society and the discontinuance of its "Memoirs," the *American Journal of Science and Arts*, first appearing in July, 1818, under the direction of Benjamin Silliman, Sr., offered to American chemists during the next half-century almost the only opportunity for the publication of chemical papers. During this period the establishment of lyceums, academies, and similar organizations in different cities of the country enabled small local groups of chemists to form scientific affiliations, but the time was not ripe for the founding of a national chemical association.

The first important participation of American chemists in a national meeting was at the Convention of the Friends of Domestic Industry, which was held in New York City, on October 26, 1831, for the purpose of improving the demoralized condition of American manufactures. The Committee on Chemistry at this convention, under the chairmanship of Isaac Tyson, Jr., of Baltimore, prepared the first statistical review of American chemical industries that was ever published. Nothing resulted, however, from the 1831 convention towards effecting a national organization of chemists.

The Priestley Centennial—celebrated at Northumberland, Pennsylvania, on August 1, 1874, and described in this volume by several of the attending chemists—was the first important solely chemical meeting of a national character to be held in the United States. The Northumberland celebration was in some respects an international event, for it was attended not only by chemists from sixteen different states of the Union but also by representatives from Canada and Great Britain. There was also a friendly interchange of cablegrams between committees in the two widely separated homes of Priestley in Birmingham, England, and in Northumberland, Pennsylvania. It is largely to the inspiring influences which emanated from the Priestley Centennial that the AMERICAN CHEMICAL SOCIETY owes its origin.

An item of outstanding importance on the program of the Priestley Centennial meeting was the historical address of Benjamin Silliman, Jr., upon "American Contributions to Chemistry."[1] This was the first attempt to give a comprehensive review of the developments in American chemistry and Silliman's work was so thoroughly performed that future writers upon the native origins of our science must always refer to his essay.

The first notable review of progress in American chemistry, to be published under the auspices of the AMERICAN CHEMICAL SOCIETY, was an address upon "The American Chemist" which G. C. Caldwell, of Cornell University, delivered as retiring President of the AMERICAN CHEMICAL SOCIETY at Pittsburgh, on December 28, 1892. This address[2] gives a general survey of the developments of chemistry in America during each decade of the previous century.

At the Twenty-fifth Anniversary of the AMERICAN CHEMICAL SOCIETY, held at New York City on April 12 and 13, 1901, under the presidency of F. W. Clarke, there was presented a special

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[1] *American Chemist*, **5**, 70–114, 195–209, 327–28 (1874).

[2] *J. Am Chem. Soc*, **14**, 331 (1892).

program of papers, reports, and addresses, which were afterwards assembled and printed as a supplement of 168 pages to THE JOURNAL. This volume contains: (1) a general account of the Twenty-fifth Anniversary celebration; (2) an essay upon "Chemical Societies of the Nineteenth Century" by the well-known bibliographer and historian of chemistry, Henry Carrington Bolton; (3) a "History of the American Chemical Society" by the Secretary, Albert C. Hale; (4) a "List of Officers and General Meetings of the American Chemical Society;" (5) a paper upon the "Organization and Development of the Chemical Section of the American Association for the Advancement of Science" by Marcus Benjamin; (6) brief reports by various members and referees of the Census Committee, under the chairmanship of Charles Baskerville, upon the progress and development of chemistry in America during the preceding quarter-century—organic chemistry being reviewed by W. A. Noyes, physical chemistry by Louis Kahlenberg, agricultural chemistry by C. L. Parsons, and the teaching of chemistry in schools by Rufus P. Williams; (7) an account of the "Formation of the American Chemical Society" by one of its charter members, C. F. Chandler; (8) an address upon "The Dignity of Chemistry" by H. W. Wiley; and (9) a list of persons registered as attending the Twenty-fifth Anniversary meeting.

The special Journal Supplement, commemorating this quarter-centennial of the AMERICAN CHEMICAL SOCIETY, not only gives the reader a comprehensive account of the activities of the SOCIETY between 1876 and 1901, but it also indicates the hopes and aspirations which some of its members entertained, at the opening of this twentieth century, regarding the future growth of chemistry in America. H. W. Wiley, at the close of his address on "The Dignity of Chemistry," predicted what the situation would be in 1976 in the following words:

> On April 12, 1976, will be celebrated the Centenary of our SOCIETY and shortly thereafter the bicentennial of our national independence May I drop for a moment the role of chemist and assume that of prophet? Our country will have then about 225,000,000 inhabitants. Our foreign export trade will amount to more than $5,000,000,000 annually. The revenues and expenditures of our Government will each reach the annual sum of $4,000,000,000. The average yield of wheat in the United States will be nearly 25 bushels per acre, and the average yield of other field crops be proportionately greater than now.
>
> Diversified manufacturing industries will flourish in every part of the country, thus distributing population and encouraging agriculture. The product of a day's labor will be double that of today, thanks to new processes, improved machinery and greater skill. The condition of the artisan and the laborer will be greatly ameliorated, and the principles of the trust, which now help chiefly the capitalist, will be extended to include the working man as well. The laborer will not only have a larger daily wage, but will also share in the legitimate profits of the business.

> The advancement of chemical science will not only make the fields more productive and more easily tilled, but will also teach how their products can be more economically and easily consumed. Good roads will lead everywhere and the horse be relegated to the museum and the stable of the sportsman. New sources of energy will take the place of coal and gas, and this energy will come from the winds and the rains. The sun directly and indirectly will monopolize the power of the country, working through evaporation and precipitation and by means of electricity or some more useful force.
>
> By a general comprehension of the principles of nutrition, food will be more wholesome and more potent. The general acceptance of the principles of hygiene will make the average life of man longer and his usefulness more fruitful. Man will not only live longer, but he will be happier and practically free from the threats of enzymic, contagious, and epidemic diseases. When this SOCIETY meets on that Founders' Day, the membership will be nearly 10,000 and its organization will reach to all quarters of our imperial country.

The members of our SOCIETY who heard these words in 1901 no doubt supposed that the genial orator was giving his imagination the utmost freedom of rein. Prophecies, however, are as apt to be understated as overdrawn and we, who now look back upon Dr. Wiley's predictions, will smile at many of his conservative estimates. The foreign exports of the United States in 1920 were $8,080,480,821 and, in the less exceptional year of 1925, $4,909,847,511. The expenditures of our country in 1925 were $4,129,234,923.68. The predictions as regards diversification of manufactures, introduction of new processes, increased output of labor, larger daily wages, advancement of chemical science, more economical utilization of products, better roads, relegation of the horse, lengthening the average of human life, and the eradication of contagious diseases have already been largely realized. The membership of nearly 10,000 which Dr. Wiley predicted for Founders' Day in 1976 was passed in 1917, when the number of members of the AMERICAN CHEMICAL SOCIETY increased to 10,603. At the present writing the membership is 14,808. While a few of Dr. Wiley's predictions, such as number of inhabitants, yield of wheat per acre, and utilization of solar energy, still await realization, the main criticism of his prophecy is that he did not advance the date of fulfilment from the Centennial to the present Semicentennial celebration of our SOCIETY.

The American chemists of the present year look back with condescension upon some of the mistaken opinions of their scientific forebears of 1876. It is certain that there will be a similar attitude upon the part of the members of our SOCIETY in 1976 with regard to some of the ideas which are included in the reviews of the present Semicentennial publication. Such changes of opinion the chemists of America gladly accept as the evidence of progress, bearing in mind the sentiment of the old adage:

We think our fathers fools, so wise we grow:
Our wiser sons, no doubt, will think us so.

There will be present at this Fiftieth Anniversary several members who took part in the establishment of the AMERICAN CHEMICAL SOCIETY in 1876; there will also be in attendance a few members, in their early twenties, who will have the good fortune to participate in the celebration of the Centennial meeting in 1976. Let us hope when these younger chemists take part in this distant event that they will transmit to their associates a kindly remembrance of the men who, in their faith and confidence, helped to found the AMERICAN CHEMICAL SOCIETY and of those who, by their energy and coöperation, have brought it to its present state of advancement.

At the Los Angeles meeting of the AMERICAN CHEMICAL SOCIETY in August, 1925, a committee was appointed for the Historical Program of the Fiftieth Anniversary, consisting of C. A. Browne, chairman, George L. Coyle, F. B. Dains, L. C. Newell, and Edgar F. Smith. The committee considered the best means of commemorating the Semicentennial of the SOCIETY to be the issuance of another special supplement of THE JOURNAL which should give: (1) accounts of the origin, foundation, and development of the SOCIETY by some of the members who took an active part in these early movements; (2) a general statement of the activities of the SOCIETY; and (3), reviews of progress in various branches of chemistry in America during the half-century of the SOCIETY'S existence.

Various obstacles have prevented the committee from making the details of this program as complete as originally intended. In addition to the reviews of progress contained in the present volume it was hoped to include surveys of the work which American chemists have performed in the fields of analysis, apparatus, pharmacy, constants, and other branches of the science, but unfortunately the limitations of time, delays, and other unavoidable contingencies, which always occur in the preparation of such a work, have interfered in carrying out certain phases of the original plan. It should also be stated that the reviews which have been prepared for the present work are in no instance complete, for the requirements of space prevented the contributors from mentioning many deserving lines of work. For these and other unpreventable omissions in the volume the committee and their collaborators hope for the lenient judgment of the members and friends of the SOCIETY.

In conclusion, the committee desires to express its appreciation to those members of the SOCIETY—too numerous to be mentioned by name—who, by supplying data, lending photographs, offering suggestions, and coöperating in other ways, have greatly assisted in the preparation of this volume. For financial support in the publication of this work a special debt of gratitude and the thanks of the AMERICAN CHEMICAL SOCIETY are due to the Chemical Foundation and to its president—Francis P. Garvan.

C. A. BROWNE, *Chairman*
Committee for the Historical Program of the Fiftieth Anniversary of the American Chemical Society

WASHINGTON, D. C.
July 20, 1926

CONTENTS

PART I

ORIGINS AND DEVELOPMENTS OF THE AMERICAN CHEMICAL SOCIETY

1876–1926

PART II

REVIEWS OF PROGRESS IN VARIOUS BRANCHES OF CHEMISTRY IN AMERICA

1876–1926

ILLUSTRATIONS

PART I

ORIGINS AND DEVELOPMENTS OF THE AMERICAN CHEMICAL SOCIETY

1876–1926

CHAPTER I

THE PRIESTLEY CENTENNIAL

BY SAMUEL A. GOLDSCHMIDT

In the April, 1874, number of the *American Chemist*, Dr. H. Carrington Bolton, an instructor in the Columbia College School of Mines, suggested that appropriate notice be taken of the approaching centennial anniversary of the discovery of oxygen by Priestley, on August 1, 1774. Prof. Rachel L. Bodley, of the Women's Medical College of Pennsylvania, proposed that the celebration be held at Northumberland, Pennsylvania, where Priestley passed the latter portion of his life. He was an advanced Liberal, who, soon after the breaking out of the French Revolution, was driven from Birmingham, England, by a mob, which set fire to his house, destroying his laboratory and much of his library.

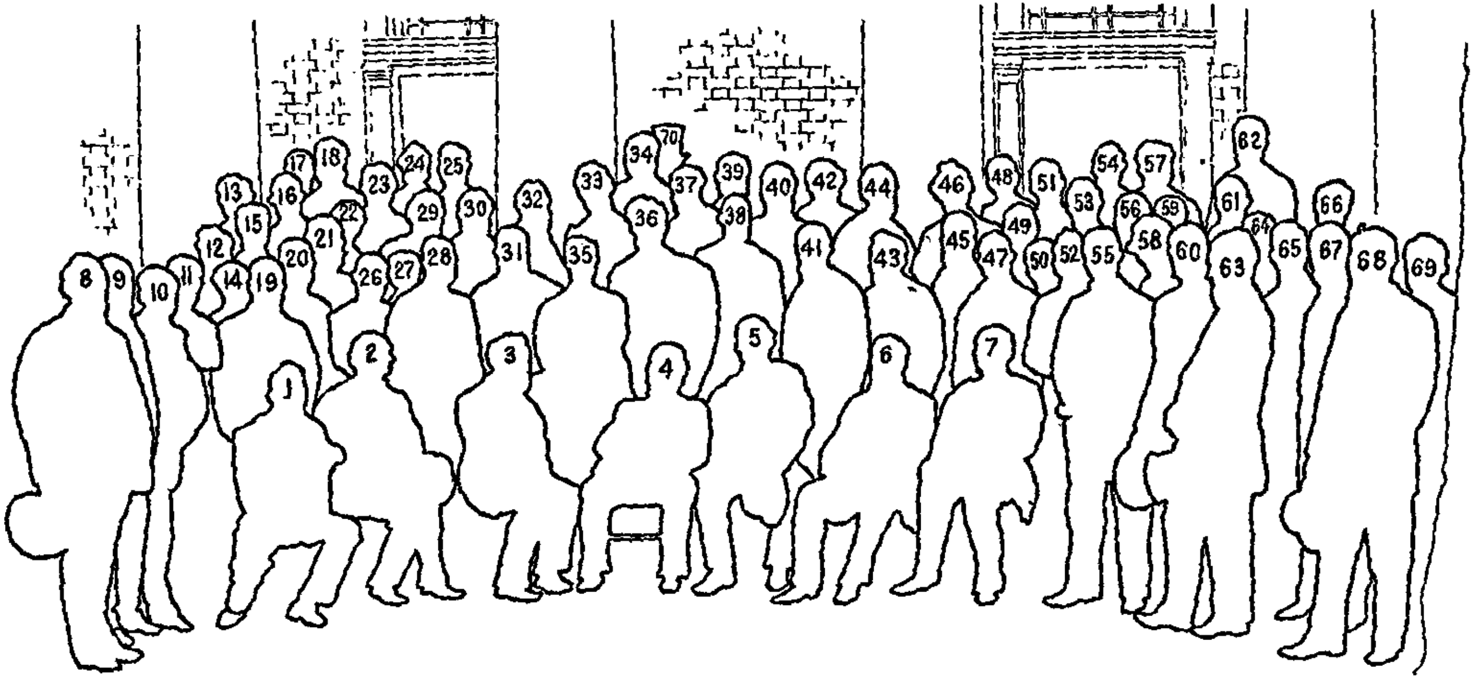
At a meeting on May 11 at the Lyceum of Natural History, the then leading scientific society of New York City, under the presidency of Prof. J. S. Newberry, appointed a committee of five members to take suitable action upon Dr. Bolton's suggestion. As a result, a circular, signed by thirty-seven of the leading chemists of the country, was issued, calling for a meeting to be held at Northumberland, on July 31, 1874.

At 9:00 A. M. on that day, seventy-seven chemists, many accompanied by ladies, met in the public school building of the little town upon the Susquehanna River. The organization was effected with Prof. C. F. Chandler as chairman and thirteen of the most distinguished chemists of the country as vice presidents. Dr. Chandler, conducted to the chair by Dr. Joseph Priestley, great grandson of the discoverer, made the opening address. Cablegrams were exchanged with Birmingham, where the unveiling of a statue took place the next day.

The following papers were then read: "The Life and Labors of Priestley," by H. H. Croft, of the University of Toronto; "The Century's Progress in Theoretical Chemistry," by T. Sterry Hunt; "A Review of Industrial Chemistry," by J. Lawrence Smith;

Group of Chemists at the Joseph Priestley Centennial of Chemistry, Northumberland, Pa., August 1, 1874

(This first photograph of a group of American chemists was taken by L. H. Laudy of Columbia College School of Mines)



1—B. S. Hedrick
2—E. N. Horsford
3—T. S. Hunt
4—J. L. Smith
5—B. Silliman
6—H. Coppée
7—Rev. T. R. Pynchon
8—Thos. Lyon
9—Conyers Button
10—
11—
12—W. M. Iles
13—
14—E. J. Hallock
15—W. H. S. Thorburn
16—John A. Church
17—
18—S. St. John
19—H. C. Bolton
20—C. F. Chandler
21—E. Waller
22—Arthur Macy
23—H. G. Torrey
24—E. L. Youmans
25—W. K. Kedzie
26—C. A. Joy
27—M. S. Thompson
28—S. P. Sharples
29—
30—
31—J. Priestley
32—S. H. Douglass
33—J. M. Maisch
34—R. C. Kedzie
35—M. B. Priestley
36—David Taggart
37—F. Hoffmann
38—E. T. Cox
39—C. G. Wheeler
40—
41—
42—
43—P. W. Bedford
44—W. W. Daniels
45—H. B. Nason
46—A. P. S. Stewart
47—T. G. Wormley
48—F. W. Clarke
49—A. A. Breneman
50—C. S. Allen
51—
52—
53—H. Endemann
54—
55—P. Frazer, Jr.
56—A. H. Gallatin
57—C. H. Chandler
58—Traill Green
59—
60—W. H. Chandler
61—
62—J. P. Remington
63—
64—E. W. Hilgard
65—A. R. Leeds
66—
67—T. M. Drowne
68—P. H. Vander-Weyde
69—
70—

COLUMBIA COLLEGE SCHOOL OF MINES GROUP AT THE JOSEPH PRIESTLEY CENTENNIAL OF CHEMISTRY, NORTHUMBERLAND, PA., AUGUST 1, 1874

(Photograph by L. H. Laudy of Columbia College School of Mines)

1—A. H. Elliot
2—C. S. Allen
3—Rev. Chas. G. Adams
4—C. A. Joy
5—E. J. Hallock
6—C. F. Chandler
7—E. Waller
8—H. C. Bolton
9—John A. Church
10—
11—C. A. Sniffin
12—W. H. S. Thorburn
13—W. M. Iles
14—Arthur Macy
15—Milton S. Thompson
16—Louis H. Laudy
17—Margaret W. Chandler (Mrs. Chas. Pellew)
18—S. A. Goldschmidt
19—Mrs. C. F. Chandler

and "American Contributions to Chemistry," by Benjamin Silliman. The latter contained a list of names and papers covering fifty-seven pages of the report of the meeting in the August-September and December numbers of the *American Chemist.*

On August 1 ceremonies were held at Priestley's grave. Owing to the illness of Joseph Henry, President Henry Coppée, of Lehigh University, made the address.

CHEMICAL APPARATUS OF JOSEPH PRIESTLEY (1733–1804) EXHIBITED AT THE CENTENNIAL OF CHEMISTRY, NORTHUMBERLAND, PA., AUGUST 1, 1874

(Photograph by L. H. Laudy of Columbia College School of Mines)

In the afternoon, Persifor Frazer, Jr., of the University of Pennsylvania, suggested that steps be taken to bring together all the chemists of the country in an "American Chemical Society." After a lively debate with J. Lawrence Smith, F. W. Clarke, E. N. Horsford, E. T. Cox, Benjamin Silliman, and P. H. Vander-Weyde in opposition, mainly upon the supposition of the lack of a sufficient number of chemists in the country to support such a society, Dr. Bolton offered as a compromise that the American Association for the Advancement of Science be requested to form a chemical section. The subject, however, laid quiescent for quite a time but, owing to Dr. Chandler's constant efforts, a meeting of chemists was held in New York in April, 1876, at which the AMERICAN CHEMICAL SOCIETY was organized.

Among the interesting exhibits shown at the centennial meeting in Northumberland was much of Priestley's apparatus, together with letters from Lavoisier and others relating to the discovery of oxygen.

After the adjournment of the meeting to August 1, 1974, an album with photographs and signatures of those present was sent to Northumberland for preservation until the next centennial should be observed. Photographs were taken by L. H. Laudy, of the Columbia College School of Mines, of views in the town, Priestley's house, apparatus, and grave, as well as of the assembled chemists, the original plates of which are now in the Columbia University library.

There was no hotel in the little town, so the visitors were entertained in the homes of the residents. No efforts were spared to make their stay agreeable and the occasion a memorable one. Memorable, indeed, as from this meeting sprang the present SOCIETY, the largest and strongest scientific organization in the world.

[EDITOR'S NOTE.—*A short time before his death, Prof. Stephen P. Sharples (1842–1923) of Cambridge, Massachusetts, a charter member of the AMERICAN CHEMICAL SOCIETY, mailed the editor a few reminiscences of the Priestley centennial of chemistry compiled from notes which were written down by him immediately after the meeting in Northumberland. His recollections give a vivid picture of the gathering and are here inserted with a few slight editorial changes.*]

In April, 1874, Dr. H. Carrington Bolton, of the Columbia School of Mines, proposed that the chemists of the country should hold a reunion that summer, it being just one hundred years since Dr. Joseph Priestley discovered oxygen and prepared the way for the many brilliant discoveries that have been made in modern times. Chemists over the country seemed to unite with the idea, and finally, at the suggestion of Prof Rachel L. Bodley of Philadelphia, Northumberland was chosen as the place of meeting.

Wishing to join in this tribute of respect to one of the pioneers of our science, I took my seat in the car of the Pennsylvania Railroad on July 30, 1874, and was soon traveling westward over their splendid road. On the cars I found plenty of friends who, like myself, were bound for Northumberland. At Harrisburg we were joined by still others. An interchange of greetings and renewals of old acquaintances, for some of us had not met for ten years, made the way seem short. About seven o'clock we arrived in Northumberland where we were met by a committee of the citizens who hospitably threw open their doors and invited us to their houses.

On the next morning, July 31, the first meeting was held. This was opened by an address of welcome from Col. David Taggart, and was followed by some routine business Then came the address of the morning by Prof H. H. Croft, of University College, Toronto, who gave us an account of the life and labors of Dr. Priestley.

Dr. Priestley was one of the most remarkable men of his time. He was a theologian, politician, chemist, and physicist, and as a linguist has been surpassed by few. In all that he did he displayed the same restless energy, the same disregard of the opinions of others, and the same determination to insist on what he believed to be the truth. His quarrels with others were innumerable and were the occasion of a vast amount of discomfort While his theoretical views in regard to chemistry have been abandoned by modern chemists, his discoveries yet remain as some of the most brilliant ever made. He was driven from his home at Birmingham, England, by a mob which destroyed his library, and came to this country to find the liberty he could not enjoy at home. One of the most moral and upright men in the community, he was, on account of the opinions he held or was supposed to hold, one of the most unpopular, and persecution did not cease even in this country, although he was not personally molested.

After the close of the address Prof. E. N. Horsford read some exceedingly interesting letters from Priestley to Judge Thatcher of Maine, in which theology and chemistry are strangely mixed.

Following this, some time was spent in inspecting the house built by Dr. Priestley and in looking at some of his apparatus. The group of attending chemists was then photographed by L. H. Laudy, of the Columbia College School of Mines. In the afternoon we again assembled to listen to an address by T. Sterry Hunt upon theoretical chemistry and the different phases which it has undergone in the last one hundred years.

After an early tea the party proceeded to Priestley's grave, which is beautifully situated on the hill overlooking the valley of the Susquehanna. Dr. H. Coppée, president of Lehigh University, here delivered an eloquent address summing up the results of Priestley's life. It has rarely been our good fortune to listen to an address that was so appropriate. His closing remarks were as follows:

> This is an unusual celebration, and this particularly is the strangest scene of this singular drama. This peaceful field, an acre of God, at this most charming evening hour, happily suggested by a lady chemist; these surrounding hills, this gleaming river, which lend breadth and beauty to the landscape; this distinguished assemblage standing reverently, but not mournfully, around a grave: these do not tell us of death, but of life; breathing, varied, sunny life; not of decay, but of resurrection; not of oblivion, but of immortality. They tell us that in the inexorable past there is but a semblance of imprisonment; that the good and the true, the magnanimous and the noble, break the flimsy bonds, and come back to gladden the hearts of men, and to flourish in perennial beauty.
>
> Such are the pleasant thoughts, fancies, and yet living facts which cluster around the grave of Joseph Priestley.

In the evening Prof. J. Lawrence Smith gave an address on the progress of technical chemistry, which was listened to with great attention by a large audience from the town. The next morning (August 1), which was the centennial or "Oxygen Day," Professor Silliman delivered an address upon the history of chemistry in America, which brought the exercises to a close. The Committee on Telegraphing reported that they had sent two dispatches to England to the chemists who were assembled at Birmingham to unveil the statue of Priestley and had received one in reply. The meeting then adjourned to meet again in 1974.

It is but rarely that every circumstance unites to make as pleasant an occasion as was this centennial meeting; all personalities and all prejudices were laid aside, and all met on a common ground to do honor to the name of Priestley. The event is one that will be long remembered by those who took part in it.

. . . . . .

I wrote this account immediately after returning to West Chester, Pennsylvania. J. Lawrence Smith went with me and spent the next day (Sunday, August 2) visiting the Battle Field of Brandywine and the Serpentine Quarries near it.

As a result of the Priestley Centennial the AMERICAN CHEMICAL SOCIETY was founded a little more than a year afterwards, nearly twenty persons who were present at the meeting becoming original members of the SOCIETY and a number of others joining afterwards.

Of those present at the Centennial the following are still living (1921): A. A. Breneman, who was with me at Penn State; S. A. Goldschmidt, of New York City; C. F. Chandler, who studied at the Lawrence Scientific School; Frank W. Clarke, my desk-mate at the Lawrence Scientific School; W. G. Levison, of Brooklyn, N. Y.; Charles W. Roepper, student under me at Lehigh; S. P. Sharples.

We all continue to take an interest in chemistry and are all still acquainted. I spent a year at Lehigh under Dr Coppée as instructor in chemistry. Professor Horsford's daughters were with him at Northumberland and one of them is living here in Cambridge.

S. P. SHARPLES

CHAPTER II

THE ORGANIZATION OF THE AMERICAN CHEMICAL SOCIETY

BY WILLIAM H. NICHOLS

The first meeting for the organization of the American Chemical Society was held on the evening of April 6, 1876, in the Lecture Room of the College of Pharmacy in the old building of New York University on Washington Square. An excellent account of this meeting is recorded in the *American Chemist.*[1] As copies of that journal are rare, it has been deemed advisable to prepare an account of the incidents of that evening in permanent form, and I have been asked, as one of the two living men who were present, to make some brief notes of the occasion, which is now historic.

The gentlemen who attended, thirty-five in all, were the following:

Meinhard Alsberg
J. P. Battershall
F. M. Baumgarten
H. C. Bolton
A. Bourgognon
Arno Behr
C. F. Chandler
Paul Casamajor
Chas. A. Doremus
F. A. C. Degenhardt
Hermann Endemann
E. P. Eastwick
T. Egleston
Charles Froebel
F. A. Grund
Wm. E. Gifford
W. M. Habirshaw
Fred Hofmann
Harwick
St. Krackowizer
Fred. Kammerer
O. H. Krause
A. R. Leeds
A. R. Ledoux
L. H. Laudy
Gideon E. Moore
H. E. Niese
W. H. Nichols
Anthony Pirtz
Prochalzka
P. deP. Ricketts
Charles Rice
Chas. M. Stillwell
Waldron Shapleigh
Isidor Walz

The name of Henry Morton does not appear in this list, although I believe he was present. At any rate, he took a most active part in the early work of the Society, and was one of the signers of the call for the first meeting. Messrs. Amend, Goldmark, Sticht, and Wendt sent letters regretting their inability to attend, but promising to join the society to be organized.

The chair was taken by Professor Chandler, who introduced the subject in his usual happy vein. In the report of his re-

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[1] *American Chemist*, **6**, No. 11 (May, 1876).

marks he is quoted as saying that he had been astonished to find that there were about one hundred and ten chemists in New York and neighboring cities whose training and pursuits rendered them fit to be members of a chemical society. I remember being just as much astonished when I learned of that large number. Chemists in those days had few opportunities to meet their fellows, other than college or business associates.

As stated by Dr. Chandler, among the objects of the SOCIETY was the securing of rooms which would be open in the day and evening and the establishment there of a reference library and a chemical museum. With one hundred members in sight, and an income of five hundred to one thousand dollars a year, this seemed like a large contract, but with the exception of the museum, we must admit he was not overoptimistic.

The meeting was fortunate in having for its secretary Dr. Isidor Walz, who became its first elected secretary and one of its most brilliant members. He was not strong physically, but was one of the most potent factors in the success of the SOCIETY in its earlier days. Unfortunately, he died less than ten years after its formation. At the organization meeting he made an excellent and well-considered address on the desirability of forming such a national society, and also expressed his astonishment to find that there were nearly, if not quite, one hundred chemists in the neighborhood of New York City who might properly be admitted to membership. The notice of the proposal to form a local society is given below:

New York, January 22, 1876.

Dear Sir:

For some time past many chemists of this city and vicinity have felt the want and deplored the absence of an association, such as exists among other professions, which would lead to a better understanding and a closer acquaintance among its members, in which scientific and practical subjects relating to our special science might be discussed, and means devised in the common interest of the profession. Widely scattered as the chemists in this neighborhood are, such an association would become the center of a pleasant personal intercourse, and of an interchange of views, experiences, and researches which would benefit all concerned.

The undersigned, believing the present an opportune time for establishing a "Chemical Society" in New York, respectfully invite your cooperation, and would be pleased to receive an early expression of your views on the subject. As soon as a sufficient number of assenting replies have been received, it is proposed to call a meeting for the purpose of forming a permanent organization.

CHAS F. CHANDLER
W. M. HABIRSHAW
H. ENDEMANN
M. ALSBERG
HENRY MORTON
ISIDOR WALZ
FRED HOFMANN
P. CASAMAJOR

In response to this circular, addressed to the chemists of New York City and vicinity, about forty favorable verbal or written assurances of interest and coöperation were received. Gratified by this unexpected interest, the committee decided to make an attempt to form a national, instead of merely a local society, and to that end issued the following circular to a much enlarged list scattered over the country:

New York, March 22, 1876.

Dear Sir:

Several weeks ago the undersigned issued an invitation to the chemists of this vicinity, requesting their coöperation toward the organization of a local chemical society. The response was so unexpectedly satisfactory, that on further consultation it was deemed opportune to attempt the formation of a national society, somewhat on the plan of those in such successful operation in France, Germany, and England. It is believed that the existence of such a society in this country would prove a powerful and healthy stimulus to original research among us, and that it would awaken and develop much talent now wasting in isolation, besides bringing the members of the association into closer union, and ensuring a better appreciation of our science and its students on the part of the general public. Guided by these considerations, we have, in consultation with other members of the profession, drafted the accompanying Constitution and By-Laws, which we submit respectfully to your kind consideration.

Among the objects contemplated are the fitting up of permanent rooms as the headquarters of the society, and in connection therewith the establishment of a library of reference, and the gradual collection of a chemical museum. It is also proposed to hold at least one meeting in each year outside of this city, at such a time and in such a place as to make attendance on the part of non-resident members more convenient and representative.

The proceedings of the society will be published and sent to the members.

If these views and objects meet with your approval, please sign and return the postal card enclosed.

Chas. F. Chandler
W. M. Habirshaw
H. Endemann
M. Alsberg
Henry Morton
Isidor Walz
Fred Hofmann
P. Casamajor

This circular was accompanied by a copy of the suggested Constitution and By-Laws which the committee prepared, modeled on those of the English, French, and German chemical societies. The response to this circular was very heartening, and on March 27, 1876, an organization meeting was called for April 6, which was attended by those noted on page 11. The wording of this notice follows:

New York, March 27, 1876.

Dear Sir:

A meeting for organizing the American Chemical Society will be held on Thursday evening, April 6, 1876, at 8 P. M , in the Lecture Room of the College of Pharmacy, University Building, corner Waverley Place and University Place.

Your attendance is earnestly requested

Chas. F. Chandler
W. M. Habirshaw
H. Endemann
M. Alsberg
Henry Morton
Isidor Walz
Fred Hofmann
P Casamajor

The first two speakers at this meeting, Prof. T. Egleston and Dr. H. Carrington Bolton, voiced the thought that the time was not opportune, and that the formation of the SOCIETY should be postponed a few years. In this judgment Prof. A. R. Leeds subsequently concurred. As I recollect, the balance of the meeting was overwhelmingly in favor of launching the craft, and proceeded to do so. From this point on, the action was unanimous. The Constitution and By-Laws were adopted. A nominating committee was appointed, and shortly afterward returned to the room and reported a ticket which, with slight modifications, was elected at the adjourned meeting, April 20.

President:
John W. Draper
Vice Presidents:
J. Lawrence Smith
Frederick A. Genth
E. W. Hilgard
J. W. Mallet
Charles F. Chandler
Henry Morton
Corresponding Secretary:
George F. Barker
Recording Secretary:
Isidor Walz
Treasurer:
W. M. Habirshaw
Librarian:
Paul Casamajor
Curators:
Edward Sherer
W. H. Nichols
Fred Hofmann
Committee on Papers and Publication:
Albert R. Leeds
Hermann Endemann
Elwyn Waller
Committee on Nominations:
E. P. Eastwick
Meinhard Alsberg
S. St John
Charles Froebel
Charles M. Stillwell

E. P. Eastwick presided at this meeting.

Although for a long time the librarian and curators did not have much to do, they assumed the duties of their offices with as much enthusiasm as any of the others. The curators gradually faded out of the picture, however, for lack of occupation.

At this second meeting it was proposed that in addition to the regular meetings more informal gatherings of the resident members be held, which would tend to bring them into closer intercourse and enable them to discuss matters of relatively minor importance not suited to the dignity of the regular sessions. This proposal was carried and was followed by many informal gatherings, known as "conversaziones," which were of the greatest value at this early stage. I think it would not be too high a flight of the imagination to conclude that these "conversaziones" were the cause of the foundation and success of The Chemists Club of New York.

It is difficult out of such a list to pick a few for special note. Some, such as Chandler, Doremus, Ledoux, and Ricketts, were with us nearly down to the present time, and were generally known to the membership of the SOCIETY. Of the remainder, many passed away long ago.

I have already alluded to Dr. Walz, to whom the SOCIETY owes much. Dr. Meinhard Alsberg, the father of one of our distinguished members, was a man of much force and ability. He was works manager and chemist of an important manufacturing chemical concern.

Dr. Arno Behr was a sugar chemist of note. He subsequently cast his lot with the growing corn products industry, and became widely known as an inventor of several important processes and substances. For this work he received the Perkin Medal of the American Section of the Society of Chemical Industry. Paul Casamajor was also a sugar chemist, although he did not by any means confine his work to his principal line. A short time before his death he told me that he had discovered a certain cure for whooping cough which he was soon to give to the world. Unfortunately, he also experimented in mushrooms, and possibly from that cause died in a cab while crossing the East River Bridge, before he had published the formula of the whooping cough specific.

Dr. Endemann had the honor of presenting the first paper to the SOCIETY. It was a long one, and the discussion lasted until nearly midnight, which made it necessary to postpone two other papers announced for that evening.

W. M. Habirshaw, who for a long time was Treasurer of the SOCIETY, was a public chemist with a laboratory in the downtown district. He was a most genial man, and endeared himself to all who met him.

Dr. A. R. Leeds was a professor at Stevens Institute, and a man of very high attainments. Dr. Gideon E. Moore had the misfortune to be stone-deaf. In conducting a conversation with one, he always presented a pad on which to write the question or the reply. He was a brilliant chemist. Dr. Shapleigh was the handsome man of the gathering, and was very popular.

Dr. Henry Morton was president of Stevens Institute. One very stormy night, shortly after the formation of the SOCIETY, he invited as many as desired to visit the laboratories at Hoboken and inspect a curious instrument which seemed to have some possibilities. This instrument was the telephone.

Waller was the most distinguished member of the meeting He was a man of great learning and had done much work in abstracting for the *American Chemist.* Stillwell was a very able analyst, his laboratory was down town, and he was called upon to decide many references. Eastwick was a member of the firm of Havermeyers & Eastwick, and a man of prominence. For a number of years he lived in Florence, Italy, in which city I believe he died last winter.

Of the company gathered at the organization meeting, H. E. Niese and the writer are all who remain.

The first out-of-town meeting was held, shortly after the organization of the SOCIETY, at Philadelphia, where we entertained the delegates from foreign countries to the Centennial Exposition. The dinner was at the Union League Club, and was really a remarkable occasion. I regret that I cannot find a list of our distinguished guests.

The whole feeling and outlook of the young SOCIETY cannot be expressed better than by Dr. John W. Draper in the concluding words of the first presidential address:

> Let us continue our labor unobtrusively, conscious of the integrity of our motives, conscious of the portentous change which is taking place in the thought of the world, conscious of the irresistible power which is behind us! Let us not return railing for railing, but above all, let us deliver unflinchingly to others the truths that Nature has delivered to us!
>
> The book of Nature! Shall not we chemists, and all our brother students, whether they be naturalists, astronomers, mathematicians, geologists, shall we not all humbly and earnestly read it? Nature, the mother of us all, has inscribed her unfading, her eternal record on the canopy of the skies. She has put it all around us on the platform of the earth! No man can tamper with it; no man can interpolate or falsify it for his own ends. She does not command us what to do, nor order us what to think. She only invites us to look around. For those who reject her, she has in reserve no revenges, no social ostracism, no Index Expurgatorius, no auto-da-fé! To those who in purity of spirit worship in her heaven-pavilioned temple, she offers her guidance to that cloudy shrine in which Truth sits enthroned, "dark with the excess of light!" Thither are repairing, not driven by tyranny, but of their own accord, increasing crowds from all countries of the earth, conscious that whatever their dissensions of opinion may heretofore have been, in her presence they will find intellectual concord and unity.

CHAPTER III

THE EVOLUTION OF THE AMERICAN CHEMICAL SOCIETY

BY FRANK WIGGLESWORTH CLARKE

In August, 1873, the American Association for the Advancement of Science met at Portland, Maine. At that time the Association was divided into two sections: Section A, devoted to the mathematical and physical sciences; and Section B, which covered the biological or natural history sciences. Chemistry, of course, fell in Section A, and was not strongly represented at the Portland meeting. The retiring president of the Association was, however, a chemist—J. Lawrence Smith—who, unfortunately, was not present at the meeting. His retiring address was read by the secretary, F. W. Putnam.

Apart from that, only six distinctively chemical papers were read at the Portland meeting; four of them related to the chemistry of soils; and two to industrial chemistry. Among the few chemists present I recall the following names: G. F. Barker, F. W. Clarke, E. W. Hilgard, T. S. Hunt, S. W. Johnson, S. P. Lattimore, William McMurtrie, C. E. Munroe, R. B. Warder, and H. W. Wiley. There were probably others, but of that I am not sure.

On the evening of August 25, 1873, a small group of these chemists met together to discuss the possibility of a better representation for chemistry in the American Association. Professor Lattimore acted as chairman, with C. E. Munroe as secretary. It was decided to ask the governing body of the Association for permission to form a subsection of chemistry within Section A, and that permission was granted. A first step toward the organization of American chemists had been taken.

It is only fair, however, to admit that there were much earlier attempts to form chemical societies in the United States, but the results were not permanent. The Chemical Society of Philadelphia was founded in 1792, and seems to have existed for about seventeen years. It was apparently revived in 1811 as the Columbian Chemical Society of Philadelphia, and in 1821 the Delaware Chemical and Geological Society was organized at Delhi, Delaware County, New York. These societies, small and feeble as they were, are interesting as having antedated all the distinctively chemical organizations abroad. The Chemical Society (London) was founded in 1841; the Société chimique de France in 1857; the Deutsche Chemische Gesellschaft in 1867; and that of Russia in 1868. The foreign chemists were, of course, represented by membership in organizations such as the British Philosophical Society and other European academies which were much older than our small attempts in behalf of chemistry alone. In America there were also organizations in the interests of science in general, such as the American Philosophical Society, the American Academy of Sciences, and the American Association for the Advancement of Science, in which chemists took an important part.

In 1874 two more forward steps were taken. In August, 1774, Priestley discovered oxygen—one of the greatest discoveries in the history of chemistry. Driven out of England by persecution, he came to America and settled at Northumberland, Pennsylvania, where he spent the remainder of his life.

It occurred to Dr. H. Carrington Bolton that it would be well to celebrate the centennial of Priestley's discovery; and it was further suggested by Miss Rachel Bodley, herself a chemist, that the celebration might most properly be held beside Priestley's grave. These suggestions were adopted, and on August 1 seventy-seven pilgrims assembled at Northumberland. Some of Priestley's descendants who lived at Northumberland took part in the meetings, which, if I remember rightly, lasted three days.

On one of these days Dr. Persifor Frazer suggested that the time was ripe for the formation of an American chemical society; and this proposition led to some discussion, pro and con. The writer, however, called attention to the proposed subsection of chemistry within the American Association, and urged that further action should be deferred until the subsection, which was soon to have its first regular meeting, could be given a chance to establish itself. Coöperation, not competition, was desirable. This suggestion was approved, and before the month was out the American Association met at Hartford, with the new subsection as one of its most successful features. Its chairman was Prof. S. W. Johnson; there was a large attendance; and a fair number of papers were presented. The ball, thus started, kept on rolling, year by year, with the subsection of chemistry a recognized feature of the

Association, until 1881 when it was made a full section, Section C, presided over by a vice president, who that year was the late Dr. H. Carrington Bolton.

Meanwhile, during the years covered by the preceding statements, three distinctively chemical societies were organized in America: the AMERICAN CHEMICAL SOCIETY in 1876; the Cincinnati Chemical Society in the early eighties; and the Chemical Society of Washington in 1884. The AMERICAN CHEMICAL SOCIETY, the nucleus from which the present SOCIETY has developed, was incorporated under the laws of New York; and its headquarters were in the city of that name, where, until 1890, most of its meetings were held. It started with fifty-three resident, and eighty non-resident members, the latter group being pretty well scattered from New England to California. At the first meeting the President of the SOCIETY was J. W. Draper of New York, and the Vice Presidents were J. Lawrence Smith, of Kentucky; F. A. Genth, of Philadelphia; E. W. Hilgard, of California; C. F. Chandler, of New York; J. W. Mallet, of Virginia; and Henry Morton, of New Jersey. J. L. Smith, S. W. Johnson, T. Sterry Hunt, F. A. Genth, J. W. Mallet, J. C. Booth, A. B. Prescott, C. A. Goessmann, H. B. Nason, G. F. Barker, and G. C. Caldwell, all non-residents, served in the order named as Presidents of the SOCIETY.

So far the SOCIETY was national in character, but as the monthly meetings were held in New York, many chemists, who lived at great distances and therefore could not take active part in the meetings, looked upon the SOCIETY as practically local, and lost all interest in it. Although the SOCIETY published a journal, that was not enough to attract a distant membership. The best American contributions to chemistry were published elsewhere. This was not a satisfactory state of affairs, but what could be done to amend it? Should more local societies be organized in different parts of the country, with small memberships and inadequate means of publishing their proceedings; or might not some form of coöperation be found which would answer all reasonable demands?

In order to answer these questions various plans were proposed. There was much discussion and some rather selfish inertia on the part of a few chemists who were so situated that they felt no need of increasing the number of their associates. The dwellers in some of the larger and older scientific centers were indifferent or even opposed to the creation of a truly national chemical society. But the advocates of coöperation were in earnest and ignored all adverse criticism.

The first result of the agitation in favor of a national organization was to stimulate the existing AMERICAN CHEMICAL SOCIETY into greater activity. It had the name and the charter, of which it could not be deprived, but its leaders saw that there was room and need for improvement. Accordingly, they adopted the plan of holding annual meetings in cities other than New York. The first of these was held at Newport, Rhode Island, on August 6 and 7, 1890. The chemists of Rhode Island at once formed a local section of the parent SOCIETY, and the membership of the latter began to increase rapidly, although it had been steadily decreasing. The accounts of the first general meeting of the SOCIETY at Newport and of the founding of the first local section in Rhode Island are given in Chapter IV by Charles E. Munroe.

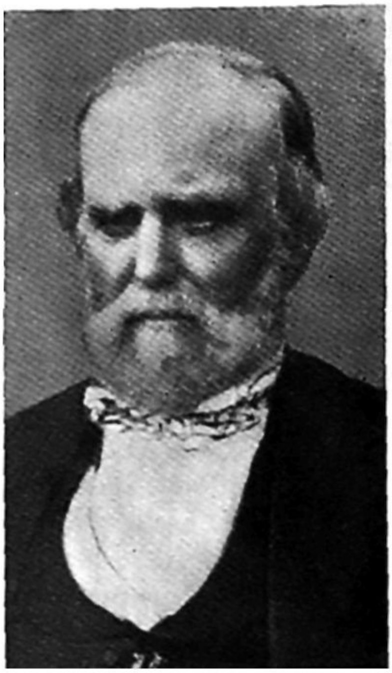
In the attempt to develop a more general organization of American chemists, the Chemical Society of Washington was especially active, and in August, 1891, a workable plan was proposed. A meeting of delegates from existing societies was held in Washington, and at this conference it was decided that the problem might be solved if the several existing organizations would unite as local sections of a national society. The name and charter of the New York Society was to be retained, with the business offices in New York. On December 9, 1891, the Board of Directors of the AMERICAN CHEMICAL SOCIETY appointed a committee to revise its Constitution and By-Laws, in conformity with the plan developed at the Washington conference. After several meetings a final report of the committee was presented, and a new Constitution was adopted on November 4, 1892. Suitable By-Laws were adopted on October 27, 1893. After several revisions the present Constitution was adopted in April, 1901.

The reorganized AMERICAN CHEMICAL SOCIETY made a promising start with four local sections; namely, New York, Rhode Island, Cincinnati, and Washington. Others were soon organized, and now the local sections number seventy, fairly covering the whole area of the United States. These sections hold their own monthly meetings, but general meetings, for the transaction of general business, are held twice a year, but seldom in the same place.

Up to this point the organization of American chemists was nearly, but not quite, complete. Section C of the American Association was still to be considered. It was active and prosperous, but independent of the AMERICAN CHEMICAL SOCIETY with which it could not be consolidated. Coöperation, however, was possible, and after much discussion and some opposition a very simple plan was adopted. The two organizations became loosely affiliated, Section C retaining its independence, but joint meetings were held in which neither party sacrificed anything, but instead gained in strength. Section C became for several years the largest section of the American Association. The first of these joint meetings was held in Washington in 1891, with Professor Barker presiding. After some years, however, the partnership was broken up, partly because of the growing size of the AMERICAN CHEMICAL SOCIETY and the difficulty of finding places to accommodate the members of the two organizations, and partly because a large number of chemists found the time of the meeting of the Association, in late summer, inconvenient.

A full account of the organization and development of the Chemical Section of the American Association for the Advancement of Science and of its relations with the AMERICAN CHEMICAL SOCIETY is given by Marcus Benjamin in the Twenty-fifth Anniversary Number of the *Journal of the American Chemical Society*, published in 1902. A complete history of the publications of the AMERICAN CHEMICAL SOCIETY, of its growth in membership, and of its numerous activities is given in Chapter V by the Secretary, Charles L. Parsons.

JOHN W. DRAPER
(1811–1882)
President 1876



J. LAWRENCE SMITH
(1818–1883)
President 1877

SAMUEL W. JOHNSON
(1830–1909)
President 1878

T. STERRY HUNT
(1826–1892)
President 1879, 1888

J. W. Draper, S. W. Johnson, and T. S. Hunt were also Charter Members; J. L. Smith and T. S. Hunt attended the Priestley Centennial in 1874. The portrait of J. L. Smith, taken from D. H. Killeffer's "Eminent American Chemists," is an enlargement from the group on page 4.

CHAPTER IV

THE FIRST GENERAL MEETING AND THE FIRST LOCAL SECTION OF THE AMERICAN CHEMICAL SOCIETY

BY CHARLES E. MUNROE

Part I. First General Meeting of the American Chemical Society at Newport, R. I., August 6–7, 1890

Like many another of the original members of the AMERICAN CHEMICAL SOCIETY who lived outside of New York City, after more than a decade of association with it, I became somewhat restive with the way that things were done in the city, and felt that my relations with the SOCIETY were quite tenuous. Hence, though situated as I was, for much of the time, remote from other chemists, I was not surprised to note that the SOCIETY was languishing, or to receive, in the fall of 1889, when it was definitely threatened by several more or less active movements throughout the country looking to the formation of a truly national organization, a copy of the call that was made on all the members to advise means by which new life might be put into the SOCIETY. In a somewhat lengthy letter, in response to this call, besides giving a review of the situation as I saw it, I suggested that the SOCIETY hold migratory meetings, such as the American Association for the Advancement of Science had held for years, and that it form local sections in various parts of the country, as the United States Naval Institute had done. I advocated these measures from my personal experience with each of these organizations and my knowledge of the success attending each.

To my gratification I learned that one or the other of these suggestions were offered by other members of the SOCIETY and that both were adopted and were later incorporated in the revised Constitution adopted June 6, 1890. I was, however, greatly surprised to be informed that, at a meeting of the Board of Directors, held July 22, 1890, a call had been issued for a general meeting to be held at Newport, R. I., on August 6 and 7, 1890, and that I had been designated as chairman of the local committee with power. Not only was the time very short but Newport seemed, in my judgment, one of the least suitable places for holding a scientific meeting.

However, the die being cast, I drew on my social relations with officers of the Army and Navy on duty at the several posts about Newport and the scientific and professional men residing there, and succeeded in forming a committee of fourteen, each of whom actively participated in the preparations for the meeting and the entertainment of the visiting chemists. Among the members of the local committee were Drs. Wolcott Gibbs and Josiah P. Cooke, professors of chemistry at Harvard University with residences in Newport, Maj. W. R. Livermore, Engineer Corps, U. S. A., in charge of the District, Comdr. T. F. Jewell, U. S. N., commanding the United States Naval Torpedo Station, Surg. C. A. Siegfried, U. S. N., representing the U. S. Naval Training Station and War College, Lieut. DeW. Wilcox, 2d Artillery, U. S. A., representing Fort Adams, together with several physicians, the principal of the high school, the secretary of the Newport Natural History Society, and some of the younger chemists of that vicinity.

Our committee meetings were held in Major Livermore's office, and I well recall the unexpressed feeling of apprehension that came over me at the session on the afternoon of August 5, as I noted the extensive preparations being made for the accommodation and entertainment of the visiting chemists. I had been notified that the President of the SOCIETY, Dr. Nason, was too ill to come and, with the exception of the Secretary of the SOCIETY, I knew of no one who was planning to attend the meeting but F. W. Clarke, William McMurtrie, and Marcus Benjamin, who were to be my house guests.

But the next morning my apprehensions were completely dissipated for quite a party, headed by the genial, efficient, confidence-inspiring Dr. Charles F. Chandler, a host by himself, came in on the Fall River boat with a party including A. A. Breneman, C. A. Doremus, L. H. Friedburg, A. P. Hallock, Charles E. Pellew, Lucius Pitkin, A. H. Sabin, J. H. Wainwright, and Elwyn Waller. Urbane Prof. John H. Appleton came down from Brown University, and Dr. H. J. Wheeler came across from the Agricultural Experiment Station at Kingston, Rhode Island. They were joined by Edwin C. Calder, Lyman C. Newell, G. W. Patterson, Charles M. Perry, and other Rhode Island chemists. Dr.

A. E. Dolbear appeared from Tufts College, E. B. Newberry from Cornell, Morris Loeb from Clark, Herbert E. Smith from Yale, and most unexpected and most welcome was Dr. E. W. Morley, of Western Reserve University, carrying his quaintly ministerial manner in a most attractive form. The records showed a signed enrollment of forty-three, representing seven states and territories, namely, Connecticut, District of Columbia, Massachusetts, New York, Ohio, Rhode Island, and Virginia.

Dr. Chandler was designated as Chairman with Prof. Albert C. Hale as Secretary. The SOCIETY was welcomed to Newport by Col. John Hare Powell, ex-Mayor of Newport and a grandson of the distinguished chemist, Dr. Robert Hare of Philadelphia, in an address delivered on behalf of the citizens of Newport, to which Dr. Chandler made a happy and most appropriate reply. Seventeen papers were presented. Two were presented by Dr. Morley in the field of atomic weight determinations, which so long occupied his attention. In reviewing the chemical work of the United States Geological Survey, Professor Clarke made the first disclosure of Hillebrand's discovery of a gas in uraninite. Naturally, from the location, there were two papers on explosives. Loeb spoke on the Gooch crucible as a silver voltameter and Doremus on fluorine for the softening of hard water. Breneman addressed the meeting on water analysis; Friedburg on resins; Dodge on grass oils; Livermore on the perissad law; Colby and Dodge on the action of nitriles on organic acids; Morgan on the extraction of indigotin from commercial indigo; Sabin on a new form of thermometer for technical use; Bartley on a new apparatus and improved method for the estimation of urea; Siegfried on Bütschli's experimental imitation of protoplasm; and Friedburg on the relative intensity of chemical force. Time was assigned for an informal discussion on the more general organization of chemists in America, which was opened by Professor Clarke with a brief review of the new movement for a proposed "Continental Society." The issue was quite actively discussed, many participating in it. The result was the appointment of a committee which played an important part in the further development of the SOCIETY, especially in reconciling differences among American chemists. It will be observed that a wide variety of topics was presented at the meetings by men of excellent standing in their specialties.

During the meeting a collection of chemical apparatus was exhibited in a room adjoining the assembly hall and the hope was expressed that in the future this feature might be more fully developed at the general meetings. This exhibit was secured by the Committee of Arrangements in New York. The committee consisted of A. A. Breneman, chairman, C. F. Chandler, William Rapp, C. F. McKenna, and J. F. Geisler, and was undoubtedly responsible for a considerable part of the attendance on the meeting.

An attractive and substantial lunch was provided each day. The afternoons were given up to witnessing demonstrations, visits of inspection, and excursions. Fortunately, the weather was perfect. At 2:30 P. M., Wednesday, government launches conveyed the members to the U. S. N. Torpedo Station, where they were met by Comdr. T. F. Jewell, U. S. N., and, through his courtesy, given an opportunity to inspect the laboratories, workshops, and the museum, in the latter of which were many interesting historic objects, as well as those of later date including the most recent forms of automobile torpedoes. The demonstrations included the firing of torpedoes in the harbor and of a considerable series of experiments with high explosives designed to develop their characteristics and to show the Munroe effect. At 4 P. M. the party was conveyed to the U. S. N. Training Station on Coaster's Harbor Island where, through the courtesy of Capt. T. W. Stanton, U. S. N., commanding, a parade of the battalion was given in its honor. Afterwards the visitors were entertained at the officers' quarters and, before leaving, inspected the barracks and drill hall under the guidance of Surg. C. A. Siegfried, U. S. N.

On Thursday, at 2 P. M., two excursions were offered: one a tour of Newport Harbor, under the guidance of Maj. W. R. Livermore, Engineer Corps, U. S. A., in his inspection launch; the other, a run of some 30 miles about Conanicut Island in the Herreshoff torpedo boat Stilletto, kindly placed at the service of the SOCIETY by Commander Jewell. This was the first high speed torpedo boat put into commission in the United States Navy. Both parties joined for a stimulating picnic lunch at Fort Dumpling, a picturesque ruin of revolutionary days, and then sailed for Fort Adams, where, through the courtesy of Col. John Mendenhall, 2d Artillery, U. S. A., commanding, a parade of a battery of artillery was viewed, and the guests given an opportunity to inspect the light and heavy artillery, and the many interesting features of the Fort.

In the evening a well-attended reception was given to the members by Prof. Josiah P. Cooke at his home. He exhibited his interesting collection of meteorites and gave a most entertaining and informing address on the Canyon Diablo meteorite and the diamonds contained in it.

The beneficial effects of this meeting on the fortunes of the SOCIETY were immediately noticeable. It established an era of good feeling and confidence. At the next regular meeting in September, instead of considering resignations, as had been too often the case, four applicants to membership were elected and twenty-one were proposed for membership or associate membership. At the October meeting these twenty-one were elected and ten proposed; at the December meeting fourteen were elected and seven proposed. The increase in membership has continued with acceleration ever since until we have become the largest chemical society in the world, but this result has been accomplished only through the efficient and devoted service of many members and officers since the time of the Newport meeting.

Part II. Formation of the Rhode Island Section of the American Chemical Society, June 4, 1891

When the members of the AMERICAN CHEMICAL SOCIETY assembled at Newport for the first general meeting of the SOCIETY, it was but natural, with the general feeling of satisfaction which pervaded the members present, that the next proposed step, viz., that of the formation of local sections, should become a subject of discussion and consideration as we met in groups during our excursions. It was generally conceded that the compact little State of Rhode Island, with three chemical centers in Brown University at Providence, the Rhode Island Agricultural Experiment Station at Kingston, the U. S. N. Torpedo Station at Newport, and many manufacturing plants at which chemists were employed, especially as it was in easy communication with the home of the parent SOCIETY, offered a particularly good opportunity for the trying out of this new feature.

To set the matter on foot, the following circular letter was sent out:

Providence, R. I.

Dear Sir:

It is believed that it will be advantageous to the chemists of Rhode Island to form a local section of the AMERICAN CHEMICAL SOCIETY here.

The Constitution of the SOCIETY, recently adopted, provides for the formation of such local sections under certain restrictions. A petition has been prepared (enclosed herewith). The intention is to secure the signatures of ten members of the SOCIETY, residing in Rhode Island; then to forward the petition to the SOCIETY in New York for approval. As soon as the petition is granted, it is intended to call a meeting of the members of the SOCIETY for the purpose of organizing the local section. We beg you to permit the signing of your name to the petition herewith enclosed. We also request that after the local section is organized, you will participate in its meetings. The general plan of the proposers is that the meetings shall be of informal character, for conference and free discussion rather than for the reading of formal papers Of course, the scope and policy of the local section when organized, will be determined by the decision of the persons joining the section.

It is believed that the local section when organized will not involve any considerable expense to members. The Constitution of the AMERICAN CHEMICAL SOCIETY provides that local sections may receive from the treasury of the SOCIETY-at-large, some fractional part of the annual dues paid by members of the local section into the general treasury. It is believed, therefore, that such an appropriation will meet all necessary expenses, such as printing, postage, and the like. If such society is organized, it is thought that there may be no expense for room rent, fuel, and lighting, as the government of Brown University will probably allow one of its lecture rooms to be used as a place of meeting by the section. It is hoped that when the section is once organized, meetings may be held occasionally in Newport and in Kingston (at the Rhode Island State Agricultural School and Experiment Station) and perhaps elsewhere.

JOHN HOWARD APPLETON
CHARLES E. MUNROE

As a result of this canvass a petition to form a section with headquarters at Providence, R. I., with permission to conduct business in the State of Rhode Island and to be known as the Rhode Island Section of the AMERICAN CHEMICAL SOCIETY, as provided in the Constitution, was addressed to the Secretary of the SOCIETY, December 31, 1890, presented by him at the regular meeting, January 2, 1891, and referred to the Board of Directors, which, on January 21, 1891, granted the petition and created the first local section of the AMERICAN CHEMICAL SOCIETY. The ten charter members were as follows:

John Howard Appleton
Edwin E. Calder
Charles A. Catlin
W. R. Livermore
Charles E. Munroe
G. W. Patterson
George E. Perkins
William R. Potter
Walter M. Saunders
H. J. Wheeler

The records of the first meeting of the Rhode Island Section held in Brown University, Chemical Laboratory Building, Thursday, June 4, 1891, at 12 noon, for purposes of organization, are as follows:

Members present

Prof. John H. Appleton
Prof. Charles E. Munroe
C. A. Catlin, Esq.
W. R. Potter, Esq.
G. M. Perkins, Esq.
Walter M. Saunders, Esq.
Prof. E. E. Calder

Prof. C. E. Munroe was elected chairman, E. E. Calder, secretary It was voted that Prof. John H. Appleton be entrusted with the care of the Charter. On motion of Professor Appleton, it was voted that the whole matter of organization be referred to a committee of five, consisting of three members from Providence, one from Newport, and one from Kingston, said committee to be appointed by the chair at his discretion.

On motion of Mr. Catlin, the following resolution was passed, to be sent to the AMERICAN CHEMICAL SOCIETY in New York at their meeting. The Rhode Island Section of the AMERICAN CHEMICAL SOCIETY, at its meeting for organization held June 4, 1891,

> *Resolved*, That it is highly desirable that the AMERICAN CHEMICAL SOCIETY participate in the conference to be held in Washington in August next, but it is not prepared to advise that its delegates commit this SOCIETY to any definite and final action on the question of the Continental Chemical Society.

An informal discussion concerning the aims and purposes of the new organization took place, and the meeting adjourned subject to the call of the chairman.
E. E. CALDER, *Secretary.*

Prof. Charles E. Munroe, chairman, has appointed the following committee to report upon a plan of organization for the Rhode Island Section of the AMERICAN CHEMICAL SOCIETY:

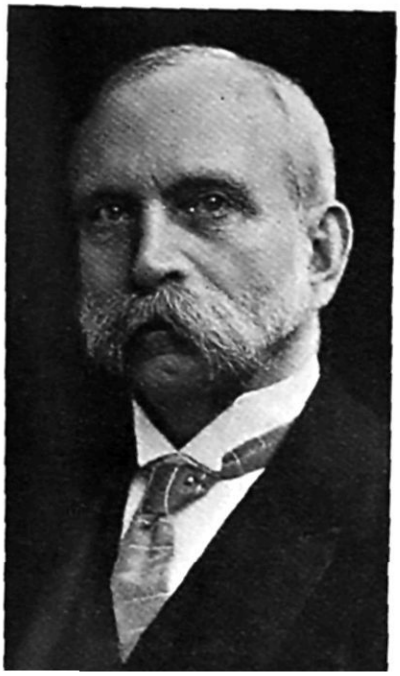
Prof. John H. Appleton   Mr. C. A. Catlin
Prof. E. E. Calder   Mr. G. W. Patterson
Dr. H. J. Wheeler

Professor Appleton is constituted senior member, and will arrange the matter of calling the committee.

Since that pleasant day in June the section has continued active and vigorous and today it numbers ninety-two members. It has always cultivated the social side, which has made attendance on its meetings especially agreeable, as well as profitable. The section celebrated the twenty-fifth anniversary of its founding in a becoming manner by a meeting, on June 3, 1916, at the Wannamoisett Country Club, which was attended by representatives of the parent SOCIETY and neighboring sections and at which Prof. Chandler made the principal address.

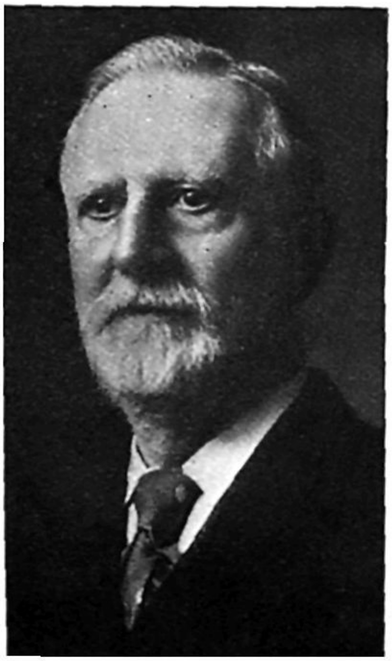
The Rhode Island Section of the AMERICAN CHEMICAL SOCIETY enjoys the distinction of being the first of seventy sections to which the AMERICAN CHEMICAL SOCIETY has granted charters. The local sections have proved of much value in maintaining the interest of the members in the objects which the AMERICAN CHEMICAL SOCIETY was created to advance and promote.

Frederick A. Genth
(1820–1893)
President 1880



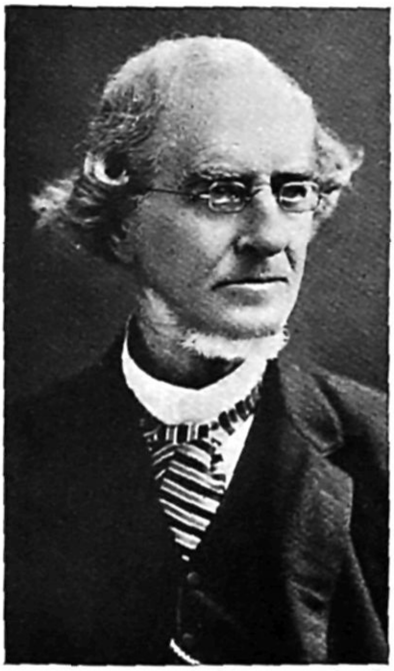
Alman & Co.

Charles F. Chandler
(1836–1925)
President 1881, 1889



Alman & Co.

John W. Mallet
(1832–1912)
President 1882



James C. Booth
(1810–1888)
President 1883, 1884, 1885

F. A. Genth, C. F. Chandler, and J. W. Mallet were also Charter Members; C. F. Chandler and J. W. Mallet attended the Priestley Centennial in 1874.

CHAPTER V

THE ACTIVITIES OF THE AMERICAN CHEMICAL SOCIETY

BY CHARLES L. PARSONS

History

In a volume commemorating the Twenty-fifth Anniversary of the AMERICAN CHEMICAL SOCIETY, printed in 1902 as a Supplement to THE JOURNAL, appears a detailed history of the first twenty-five years of the SOCIETY, by Albert C. Hale, for many years its efficient Secretary.

The petition of a group of chemists to form a subsection of chemistry in the American Association for the Advancement of Science at Portland, Maine, in August, 1873, and a gathering of chemists which met at Northumberland, Pennsylvania, at the former home and final resting place of Joseph Priestley, on August 1, 1874 (the one hundredth anniversary of his discovery of oxygen), were indications of a growing desire upon the part of American chemists to meet together at occasional intervals. A number of those who participated in these gatherings felt, however, that a separate and entirely independent organization of American chemists should be established. At a formal meeting held in New York, at the home of C. F. Chandler on January 22, 1876, a committee was formed which sent out a circular letter suggesting the establishment of such an organization. The response was so gratifying that it was determined to form a national, instead of a local, society.

Following further communications with the chemists of the country an organization meeting was held on April 6, 1876, at the old New York University Building, New York City, over which Professor Chandler presided, with Isidor Walz as Secretary. After full discussion, the meeting adjourned until April 20. On that date, the AMERICAN CHEMICAL SOCIETY was definitely organized and officers elected. John W. Draper was elected its first President, and the names of fifty-three resident and eighty non-resident chemists appear as charter members. Its first Constitution and By-Laws were adopted on that date. Of those original one hundred and eighty-three members, four, namely, J. B. F. Herreshoff, Charles E. Munroe, Wm. H. Nichols, and H. E. Niese, have maintained an unbroken connection with the SOCIETY throughout its fifty years. Two other members, S. A. Goldschmidt and Adolph Kuttroff, have also been with the SOCIETY fifty years, but they were not present at the first meeting.

Although the SOCIETY started nominally as a national organization, its meetings were so local in character, being confined to New York City, that there was little evidence of general support from American chemists until fifteen years later, when it became truly national in scope. The SOCIETY was chartered as a non-profit, non-stock corporation of the State of New York, on November 9, 1877. Its Directors could be elected only from citizens of New York state in which all business of the SOCIETY had to be transacted. Owing to this fact, and to the circumstance that the meetings were held wholly within New York City, the impression was produced upon non-resident chemists that the SOCIETY was local, rather than national, in its character and aims. Non-resident members did not come into such active intimate relations with the SOCIETY as was desirable, and accordingly there was little growth during the first years after its organization.

In 1890 an attempt was made to start another society of chemists which should be more national in character, but this appeal was met by the argument that the AMERICAN CHEMICAL SOCIETY, although small in numbers, had already acquired actual recognition and prestige, that its name and charter had a national significance, and that changes could be made in its organization which would command the active support of the great body of American chemists. As a result, a general conference was held in Washington on August 17, 1891, which was attended by delegates representing chemical societies from various sections of the country. A general plan of procedure was outlined; a new Constitution and By-Laws were proposed; a special law was drawn up and later (1895) passed in New York state which permitted the Directors of the SOCIETY to be elected without restrictions as to residence and place of meeting. After numerous conferences a complete reorganization was effected, a final report was made, and a new Constitution was adopted on November 4, 1892. Although this Constitution was an improvement over any which had preceded, it was still found to be imperfect, and another was adopted on December 2, 1897. Corresponding By-Laws went into effect on April 12, 1898.

Every step taken had been one of progress toward a truly national organization and the chemists of the country began rapidly to realize that without reference to residence they had a real part in the SOCIETY and its future. This feeling had been particularly encouraged by the new policy of holding general meetings and transacting business in numerous chemical centers. The formation of local sections, which held regular meetings, had especially fostered among chemists a feeling of broad general interest. The first of these was established at Providence, Rhode Island, January 21, 1891, and thirteen local sections were in actual operation at the time of the SOCIETY'S Twenty-fifth Anniversary.

In January, 1893, the Board of Directors accepted the proposition of Edward Hart to suspend his *Journal of Analytical and Applied Chemistry* and to take over the publication and editing of the *Journal of the American Chemical Society.* This was an important advance toward unifying the country's chemical publications, and Dr. Hart continued as editor of the SOCIETY'S JOURNAL until 1902. The editing of THE JOURNAL between 1884 and 1893 had been ably performed by A. A. Breneman who, without recompense, devoted much of his time and energy during this uncertain period to keeping the SOCIETY alive.

In 1896 an arrangement was made with Section C of the American Association for the Advancement of Science whereby the summer meetings of the two organizations of chemists were held at the same place in the same week, the first two days being given to the sessions of the AMERICAN CHEMICAL SOCIETY and the remainder to those of Section C. This arrangement continued for many years, until 1912, when circumstances necessitated its discontinuance. The AMERICAN CHEMICAL SOCIETY had then grown to such numbers that the difficulty of finding adequate meeting places obliged the two organizations, much against their will, to meet again separately. The AMERICAN CHEMICAL SOCIETY has, however, always coöperated with the American Association for the Advancement of Science, and its President and Secretary are still ex-officio members of the Council of the Association. At the end of its first twenty-five years, the SOCIETY had 1933 members, of whom 1281 were registered in local sections.

The concluding second half-century of the AMERICAN CHEMICAL SOCIETY has been a period of continued growth in membership, influence, service, and prestige. It is the largest scientific organization in the world devoted to the interests of a single science. Its membership is three times that of any other chemical organization, and its contributions to chemical literature, the most voluminous of their kind, are excelled in quality by none. The principal activities and the important developments of the AMERICAN CHEMICAL SOCIETY must be considered separately in order to be fully understood.

Publications

The advancement of chemical knowledge and the recording of chemical research and chemical practice have been the chief aim and the greatest accomplishment of the AMERICAN CHEMICAL SOCIETY. It publishes three journals, the *Journal of the American Chemical Society*, *Chemical Abstracts*, and *Industrial and Engineering Chemistry*, which are sent to all members of the SOCIETY and to many non-member subscribers. These three journals are supplied to all members of the SOCIETY without other payment than their membership dues. In their respective fields they contain more material and touch the chemical horizon more completely than any similar publications. On account of the size of their subscription lists, which exceed those of any other chemical journals, and the consequent reduction in expenses of publication, the three journals are supplied to members of the SOCIETY for about one-half the cost of any similar choice of publications in any language.

In addition to its journals, the AMERICAN CHEMICAL SOCIETY publishes two series of chemical books, one scientific, and the other technical, each with distinct editorial boards; *Chemical Reviews*, published quarterly under the auspices and editorial control of the SOCIETY; and the *Journal of Chemical Education*, published monthly by the SOCIETY's Division of Chemical Education. These are supplied to members and non-members at a nominal cost. The *Journal of Physical Chemistry* is published under the joint auspices of the AMERICAN CHEMICAL SOCIETY, the Chemical Society (London), and the Faraday Society.

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY.—Immediately upon the organization of the AMERICAN CHEMICAL SOCIETY, arrangements were made with the editors of the *American Chemist*, which was established by Charles F. Chandler in 1870, and continued until 1877, to print the Proceedings of the SOCIETY in his journal. They were also issued as separate reprints to the members of the SOCIETY during 1876–1878, and formed the first two volumes of the SOCIETY's publication under the heading, "Proceedings of the American Chemical Society, Volume 1 and Volume 2."

The *Journal of the American Chemical Society* appeared first in

1879 as an independent monthly publication. Not always during the next fifteen years was it possible to issue twelve numbers annually, but a volume was issued each year, and beginning with 1893 monthly issues have appeared to date, THE JOURNAL constantly growing in size and in quality. At the end of forty-eight years, THE JOURNAL carries annually 3300 pages of chemical research, chiefly in the fields of general, physical, inorganic, organic, and biological chemistry. Most of the contributions to pure chemistry, published in America, appear in its pages.

In addition to these records of research, THE JOURNAL contains the Proceedings of the SOCIETY and numerous reviews of books on pure chemistry and related subjects. With it, in 1897, was incorporated the *Review of American Chemical Research,* a predecessor of *Chemical Abstracts*, the first two volumes of which had already appeared as a part of the *Technology* (*Massachusetts*) *Quarterly,* of which Arthur A. Noyes was editor. It was discontinued at the end of the year 1906, *Chemical Abstracts* becoming its worthy successor. In 1914, the *American Chemical Journal,* founded and edited by Ira Remsen, was incorporated with the *Journal of the American Chemical Society.* Complete sets of THE JOURNAL are almost unprocurable.

CHEMICAL ABSTRACTS.—In January, 1907, the AMERICAN CHEMICAL SOCIETY, then having 3300 members, began the publication of *Chemical Abstracts.* The growth of chemical literature had become so great that a comprehensive abstract journal was an absolute necessity, if English-speaking chemists were to keep abreast with the chemical research of the world and to compete with the preponderant position which Germany, at that time, had gained in chemical development. *Chemical Abstracts* was established with the avowed purpose of publishing adequate abstracts of all papers of scientific and industrial chemical interest appearing throughout the world, regardless of the language in which they were printed. It has accomplished this object with a high degree of efficiency. The literature of chemistry has, however, been growing so steadily in recent years that it has become increasingly difficult to give it adequate treatment within the space limitations which the AMERICAN CHEMICAL SOCIETY'S more slowly growing income imposes. The extent of this growth of literature is shown by the following figures, which give the number of abstracts published in the past eight years:

Year	1918	1919	1920	1921	1922	1923	1924	1925
Number of abstracts	13,357	14,696	18,051	19,476	23,212	24,256	25,607	26,426

In order to continue the important policy of completeness it has been necessary, for keeping within limits, to reduce the length of abstracts. The amount of reduction is shown by figures for the average length of abstracts of papers and of patents, which follow. The unit is a page.

Year	1917	1918	1919	1920	1921	1922
Abstracts of papers	0.251	0.220	0.244	0.223	0.218	0.190
Abstracts of patents	0.108	0.099	0.115	0.107	0.098	0.086

In 1923 it became necessary to use solid composition and make other space economies so that a comparison for 1923–1925 with the period 1917–1922 is impossible. Even further reductions in the length of abstracts was necessary and, in order to save expense, use is made of every possible method of abbreviation. In spite of this drastic condensation, the 26,426 abstracts in *Chemical Abstracts* for 1925, with index, covered 4773 pages of 8-point solid composition.

Starting with an initial expenditure of only $11,606.60 in 1907, the costs of publishing *Chemical Abstracts* have continually increased until in 1925 they exceeded $100,000, which is about 35 per cent of the total expenditure of the SOCIETY.

In order that *Chemical Abstracts* may be made more useful to individuals without extensive library facilities, a list of American libraries and of the chemical journals to which they subscribe has been compiled and directions are given as to the method of procuring photographic copies of original articles and also, if necessary, of translations. In order that its influence may be as international as possible, advance galley proofs of abstracts are exchanged with the Society of Chemical Industry and the Chemical Society (London). The subscription rates of *Chemical Abstracts* are lower than what other far less complete abstract journals are obliged to require. This, and all the other journals of the AMERICAN CHEMICAL SOCIETY, are now found in all of the important libraries of the world.

While *Chemical Abstracts* has been the greatest asset of the AMERICAN CHEMICAL SOCIETY in disseminating the results of research, it has also been its greatest financial burden, owing to the curve in the productivity of chemical research rising more rapidly than the curve of the present income from American chemists. It is confidently expected that means will be found to continue and enlarge both the scope and usefulness of this important journal without increasing its cost to the chemists of the world.

In preparing chemical abstracts, each individual review is written by a chemist who is a specialist in the particular field involved. The quality of the abstracts is further safeguarded by the editorial supervision of men of high standing in their branches of chemistry, who serve as assistant editors, one or more being in charge of each of the thirty sections into which the abstracts are classified. Special attention is given to the indexing, particularly the subject index. The official index number with its separate author, subject, and formula indexes can be used with confidence as a key to the whole literature of chemistry for the period covered.

A collective index to the first ten volumes (1907–1916) of *Chemical Abstracts* has been published, consisting of two volumes, containing 1980 pages, devoted to authors; and two volumes, containing 2843 pages, devoted to subjects. A second Decennial Index covering the years 1917–1926 is in preparation and will be issued shortly. Its magnitude can be gauged somewhat by the estimate that the 3500 copies of seven volumes each to be printed will cost the SOCIETY in the neighborhood of $100,000.

Chemical Abstracts is published semimonthly and has much the largest circulation of any scientific abstract journal in the world.

INDUSTRIAL AND ENGINEERING CHEMISTRY.—This journal began publication in 1909 and has become a power in the industrial and engineering field. It is the one journal of the AMERICAN CHEMICAL SOCIETY which is financially remunerative, yielding through its advertisements a net income of approximately $70,000 a year, which has enabled the SOCIETY to publish, at a reduced cost to its members, the *Journal of the American Chemical Society* and *Chemical Abstracts*. The Industrial Journal was established to meet the demand of the industrial and engineering chemists of America shortly after the adoption by the SOCIETY of the divisional organization, which has proved so helpful in its growth and welfare.

Industrial and Engineering Chemistry, as its name implies, covers the broad field of the application of chemical science. In its columns are found contributions from the laboratories of practically every university and industrial research organization in America. This material covers a wide range of subjects, such as dyes and textiles, the metals, leather, cellulose, rubber, fertilizers, petroleum, gas and fuel, agriculture and food, medicinal products, sanitation, etc. Many papers are written from the engineering point of view; others discuss the industrial application of discoveries in pure science; while a third group deals with analytical processes or new laboratory apparatus. From time to time other features appear, such as statistical surveys of the chemical industries of this and other countries, summaries of the progress of chemistry in many industrial fields, or special articles and bibliographies by writers expert in the subjects treated. Government publications in the technical field, reviews of new books, and chemical market conditions are summarized. A special feature of *Industrial and Engineering Chemistry* is the editorial section.

In 1922 a proposal was presented to the Directors of the SOCIETY to publish *Industrial and Engineering Chemistry* in three parts, two of them to be simply a popular news edition. This was favorably considered and the News Edition was accordingly begun with the January issue of 1923. While the Industrial Journal itself appears on the first of the month, the semimonthly issues of the News Edition appear on the tenth and twentieth.

The News Edition publishes reports of scientific meetings, general news items, notes from the industrial field, changes in business connection, personal notes, and construction news. It carries also employment information for the members, and letters from correspondents in Canada, England, France, Germany, Italy, Japan, Norway, and other foreign countries. As it keeps the membership abreast of the times, it has, as was anticipated, supplied an important demand.

CHEMICAL MONOGRAPHS.—As a result of the report of a committee on compendia of chemical literature, presented at the general meeting of the SOCIETY in Buffalo, New York, in 1919, the AMERICAN CHEMICAL SOCIETY undertook, at the end of that year, the publication of two series of chemical books, one of a scientific and the other of a technical nature. This was the first serious attempt to build up a chemical literature in English without primary regard to commercial conditions. W. A. Noyes has been the editor of Scientific Monographs since 1920. John Johnston was editor of Technologic Monographs from 1920 to 1922, and since that time H. E. Howe has been the editor. Each editor is assisted by a capable board of associate editors. These books are published through a business arrangement with the Chemical Catalog Company, of New York City. Twenty-seven books have already been issued. Thirty-five unpublished treatises have been announced and others are under consideration.

JOURNAL OF PHYSICAL CHEMISTRY.—The *Journal of Physical Chemistry* was founded by Wilder D. Bancroft and edited and published by him until January, 1923, when the Chemical Foundation guaranteed its publication to the extent of $10,000 a year for five years if arrangements could be consummated to place it on an international basis. A conference was held in London on June 23, 1923, by the Secretary of the SOCIETY with representatives of the Chemical Society (London)[1] and a definite arrangement was

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[1] *J. Am. Chem. Soc.*, Proceedings, **44**, 91 (1922).

unanimously agreed to whereby the *Journal of Physical Chemistry* was to be continued under the joint auspices of the two societies, each having a representation of four members on the board, the board itself to elect the editor-in-chief. A request was later received from the Chemical Society (London) to permit the Faraday Society to join with them and nominate one of the board, which was unanimously approved. Wilder D. Bancroft was elected editor-in-chief, and accordingly for three years the *Journal of Physical Chemistry* has been continued as a journal of international character under the joint auspices of the societies above enumerated.

JOURNAL OF CHEMICAL EDUCATION.—On January 1, 1924, the Section of Chemical Education, not then organized as a division, undertook on its own financial responsibility, after the plan had been approved by the Executive Committee of the Council, the issuance of a new journal, the *Journal of Chemical Education*, which afterwards came under the auspices and direction of the Division of Chemical Education, and has been conducted with the financial aid of the Chemical Foundation upon a subscription basis. The journal has proved very successful under the editorship-in-chief of Neil E. Gordon and the business management of Erle M. Billings, and although not yet entirely self-supporting, there is every reason to believe that it will soon become so, since the number of subscribers is rapidly increasing. It has filled an important demand among the chemistry teachers in our colleges and secondary schools, bringing many of them in closer touch with the work of the SOCIETY for the development of American chemistry.

CHEMICAL REVIEWS.—*Chemical Reviews* was first published in April, 1924. It was initiated by a movement in the Division of Chemistry and Chemical Technology of the National Research Council, of which J. E. Zanetti was chairman, to provide a vehicle for the appearance of comprehensive analytical reviews, summaries, and short monographs on topics of interest to chemists. The crowded nature of the *Journal of the American Chemical Society* and the inability of the SOCIETY to give space in its pages to long articles of this character had deprived the profession of many valuable contributions. A number of such reviews having been prepared for publication, the Williams and Wilkins Company, of Baltimore, Maryland, came forward with an offer to publish them at their own risk and under their own business management, but under the absolute editorial control of the AMERICAN CHEMICAL SOCIETY. They agreed to give special rates on subscriptions to members of the AMERICAN CHEMICAL SOCIETY and affiliated organizations; to publish at least four numbers a year of 500 pages to the volume; and not to duplicate the work of any other journal of the SOCIETY. *Chemical Reviews* was accordingly assigned its own definite field and has supplemented, not supplanted, the SOCIETY's other journals. William A. Noyes, editor-in-chief of Scientific Monographs, was appointed editor-in-chief of *Chemical Reviews*, and the associate editors of Scientific Monographs and the editors of Technologic Monographs were assigned to assist him as an editorial board. Two successful volumes of *Chemical Reviews* have been completed at the time of the SOCIETY's Fiftieth Anniversary.

Organization Statistics

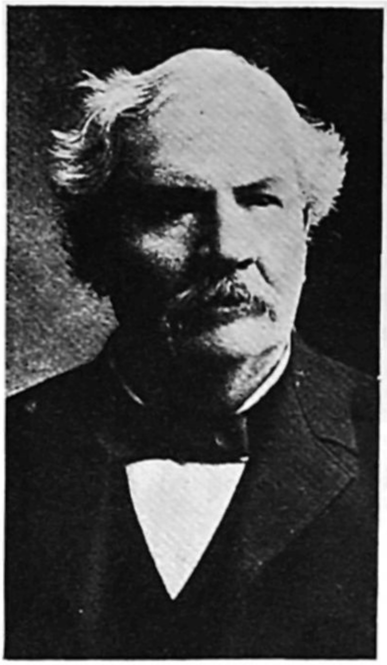
The object of the AMERICAN CHEMICAL SOCIETY from the time of its establishment has been:

> "The advancement of chemistry and the promotion of chemical research."

The results of its fifty years' work with this purpose in view are apparent to every observer. The SOCIETY has had a very large influence in bringing about the present unexcelled facilities and personnel, both in pure and applied chemistry in America. There is no country in the world in which there is a greater appreciation of the value of chemical research for the advancement of chemical knowledge and development of chemical industry. For this the AMERICAN CHEMICAL SOCIETY can justly claim much credit. The majority of its members are residents of the United States of America, but there is no geographical or national restriction, and individual chemists from nearly every civilized nation in the world are included in its membership. It has about the same number of foreign members as it had total membership at the time of its Twenty-fifth Anniversary.

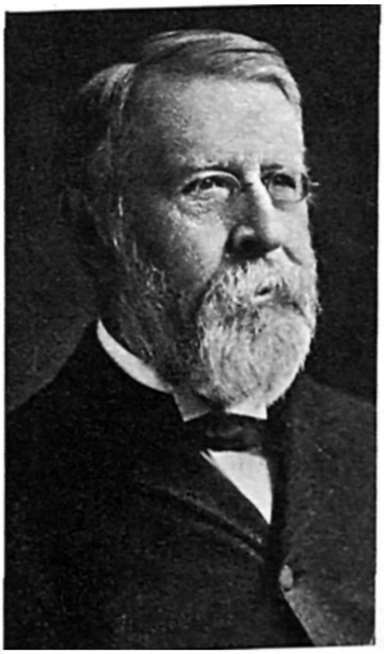
MEMBERSHIP.—Any person interested in chemistry, properly recommended by members of the SOCIETY, may be elected a member. Prior to 1903, it had associate as well as full members. General dissatisfaction in this attempt to classify the members of the SOCIETY led to its abandonment and to a much greater harmony within the SOCIETY without any loss of accomplishment or prestige. Although interest in the profession, desire for service, and good reputation are the sole requirements of membership, nevertheless those who belong to the SOCIETY are almost without exception well-trained and experienced chemists. The SOCIETY can record with pride that nearly every American chemist who

Albert B. Prescott
(1832–1905)
President 1886



Charles A. Goessmann
(1827–1910)
President 1887

Henry B. Nason
(1831–1895)
President 1890



George F. Barker
(1835–1910)
President 1891

A. B. Prescott, C. A. Goessmann, and H. B. Nason were also Charter Members; H. B. Nason attended the Priestley Centennial in 1874; G. F. Barker was Corresponding Secretary in 1876 and 1877.

has enjoyed any considerable distinction during the past fifty years has been or is an active member of the AMERICAN CHEMICAL SOCIETY. Many of them have devoted much of their time, their talents, and their best energies to administering its affairs, to shaping its policy, and to securing for it the prominent position of dignity and of influence which it now holds in the scientific world. Five hundred and ninety-eight members have retained their connection with the SOCIETY twenty-five years or more. The character of its membership can be judged from the following classification made from its latest Directory:

	Per cent
EXECUTIVES OF FIRMS AND CORPORATIONS:	
Presidents, vice presidents, secretaries, treasurers, and chairmen of boards	7 28
MANAGERIAL:	
Directors, purchasing agents, general managers, sales agents, superintendents, directors of departments, chiefs of departments, and heads of departments	17.58
TECHNICAL DIRECTION:	
Chief chemists, metallurgists, chemical engineers, and consultants	19.57
CHEMICAL DEVELOPMENT:	
Research chemists	8.97
CHEMICAL CONTROL:	
Works chemists and laboratory chemists	8 47
PROFESSORS OF CHEMISTRY	10.06
INSTRUCTORS AND TEACHERS	5.84
STUDENTS:	
Graduate and undergraduate students	5.15
CORPORATIONS, MISCELLANEOUS AND UNCLASSIFIED	17.08

The following yearly record of membership from the beginning of the SOCIETY will indicate its growth:

Membership of the American Chemical Society, 1876–1926

1876	230	1891	302	1906	3079	1921	14,318
1877	265	1892	351	1907	3389	1922	14,400
1878	256	1893	460	1908	4004	1923	14,346
1879	289	1894	722	1909	4502	1924	14,515
1880	303	1895	903	1910	5081	1925	14,381
1881	314	1896	1011	1911	5603	1926*	14,808
1882	293	1897	1156	1912	6219		
1883	306	1898	1415	1913	6673		
1884	323	1899	1569	1914	7170		
1885	255	1900	1715	1915	7417		
1886	241	1901	1933	1916	8355		
1887	235	1902	2188	1917	10,603		
1888	227	1903	2428	1918	12,203		
1889	204	1904	2675	1919	13,686		
1890	238	1905	2919	1920	15,582		

* July count

Membership dues are $15.00 a year. There is no initiation fee.

LIFE MEMBERSHIP.—Any member who pays into the general treasury at one time the sum of $300 as a commutation for dues may become a Life Member, with the privilege of being exempt from further dues and of receiving all the publications of the SOCIETY during the remainder of his life. The income from this fund is used for the payment of the member's dues during his life, and on his death the principal sum reverts to a special membership fund, the income of which may be used only for the aid of chemical research. The SOCIETY now has twenty-one Life Members, as follows:

Wilder D. Bancroft
Walker Bowman
Henry P. Busch
O. C. Collins
William F Cuming
Herbert H. Dow
S. A. Goldschmidt
Adolph Kuttroff
K. Y. Kwang
H. W. Leitch
Nariman A. Masani
Wm. P. Mason
Emerson R. Miller
Charles E. Munroe
A. G. Rosengarten
Frederic Rosengarten
George D. Rosengarten
Charles S. Roy
Albert P Sachs
Oswald Silberrad
Elihu Thomson

HONORARY MEMBERSHIP.—Any person whose achievements in chemistry may be considered as entitling him to special recognition as an authority in theoretical or applied chemistry may be elected an Honorary Member, but only in a general meeting of the SOCIETY after his name, presented in writing by ten members, has received the written endorsement of a majority of the Council, and has laid over one general meeting, or six months, in the hands of the Executive Committee. The following is a list of past and present Honorary Members of the AMERICAN CHEMICAL SOCIETY:

Honorary Members

NAME	YEAR ELECTED	NAME	YEAR ELECTED
Berthelot,* M. P. E.	1876	Lunge,* George	1901
Boutlerow,* A. M. von	1876	Ramsay,* William	1901
Bunsen,* R. W.	1876	Roscoe,* Henry E.	1901
Cannizzaro,* Stanislao	1876	von Baeyer,* Adolph	1901
Dumas,* J. B.	1876	Arrhenius, Svante A.	1905
Frankland,* Edward	1876	Nernst,** Walther	1905
Williamson,* A. W.	1876	Roozeboom,* H. W. B.	1905
Woehler,* Friedrich	1876	Thomsen,* Julius	1905
Chevreul,* M. E.	1884	Perkin,* William Henry	1906
von Hoffman,* A. W.	1884	Curie, Marie S.	1910
Kekulé,* August	1889	Dewar,* James	1910
Mendeléeff,* Dmitri	1889	Fittig,* Rudolph	1910
Stas,* J. S.	1891	Mallet,* John W.	1910
Gibbs,* Wolcott	1894	Strutt,* John Wm (Lord Rayleigh)	1910
Crookes,* William	1898		
Moissan,* Henri	1898	Van der Waals,* Johannes Diderik	1910
Van't Hoff,* J. H.	1898		
Morley,* E. W.	1900	Werner,* Alfred	1915
Ostwald,** Wilhelm	1900	Grignard, Victor	1917
Fischer,* Emil	1901	Ciamician,* Giacomo	1919

Honorary Members (*Concluded*)

NAME	YEAR ELECTED	NAME	YEAR ELECTED
Solvay,* Ernest	1920	Irvine, James C.	1926
Chandler,* Charles F.	1921	Miller, W. Lash	1926
Kestner, Paul	1921	Moureau, Charles	1926
Nichols, Wm. H.	1921	Pictet, Amé	1926
Pope, William J.	1921	Remsen, Ira	1926
Sörensen, S. P. L.	1924	Richards, Theodore W.	1926
Brauner, Bohuslav	1926	Sabatier, Paul	1926
Bruni, Giuseppe	1926	Sakurai, Joji	1926
Cohen, Ernst	1926	Smith, Edgar Fahs	1926
Donnan, Frederick G.	1926	Swarts, Frederic	1926

* Deceased
** Discontinued

CORPORATION MEMBERSHIP.—In 1909 the SOCIETY established a special membership for firms and corporations, known as Corporate Membership, at a higher rate of dues. Corporate members have the privilege of appointing a delegate to any meeting of the SOCIETY and the right to a limited number of reprints of special papers when such request is made in advance of publication. The main object of Corporate Membership is, however, to secure the active interest and patronage of the chief industrial concerns of America. In this the SOCIETY has been successful. Three hundred and eighty-two of our most important and leading chemical corporations have identified themselves officially, under this provision, with the AMERICAN CHEMICAL SOCIETY.

STUDENT MEMBERSHIP.—The Council and Directors have also voted to give special discounts to bona fide undergraduate and graduate students of chemistry, in order to assist them during this unproductive period and to interest them early in life in the aims and objects which the SOCIETY is fostering.

OFFICERS.—The officers of the SOCIETY consist of a President, one Vice President for each division of the SOCIETY, who is the presiding officer of such division, a Secretary, a Treasurer, the three editors of its basic publications, nine Directors, and a Council.

The Directors are the legal representatives of the SOCIETY and as such hold in trust and administer all the property of the SOCIETY for its use. The Directors consist of the President, Secretary, and the Treasurer ex officiis, and six Directors chosen by the Council, two each year for a term of three years, one Director being elected from each of the six regional divisions of territory into which the SOCIETY is divided. The regional Directors are nominated by the local sections within that territory, but are elected by the Council. The officers of the SOCIETY during the last twenty-five years follow:

Officers of the American Chemical Society, 1902–1926[1]

PRESIDENTS.—Ira Remsen, 1902; John H. Long, 1903; Arthur A. Noyes, 1904; Frank P. Venable, 1905; W. F. Hillebrand, 1906; Marston T. Bogert, 1907–8; Willis R. Whitney, 1909; Wilder D. Bancroft, 1910; Alexander Smith, 1911; Arthur D. Little, 1912–13; Theodore W. Richards, 1914; Charles H. Herty, 1915–16; Julius Stieglitz, 1917; Wm. H. Nichols, 1918–19; William A. Noyes, 1920; Edgar F. Smith, 1921–22; Edward C. Franklin, 1923; Leo H. Baekeland, 1924; James F. Norris, 1925–26.

SECRETARIES.—Albert C. Hale, 1902; William A. Noyes, 1903–7; Charles L. Parsons, 1907–

TREASURERS.—Albert P. Hallock, 1902–16; E. G. Love, 1917–18; John E. Teeple, 1919–

EDITORS, JOURNAL OF THE AMERICAN CHEMICAL SOCIETY.—William A. Noyes, 1902–17; Arthur B Lamb, 1918– .

EDITORS, CHEMICAL ABSTRACTS.—William A. Noyes, 1907–10; Austin M. Patterson, 1911–13; John J Miller, 1914; E. J. Crane, 1915– .

EDITORS, INDUSTRIAL AND ENGINEERING CHEMISTRY.—W. D. Richardson, 1909–10; M. C. Whitaker, 1911–16; Charles H. Herty, 1917–20; Harrison E. Howe, 1921– .

COUNCIL.—The Council is an advisory body on every matter pertaining to the general management or policy of the SOCIETY. It consists of the officers of the SOCIETY ex officiis, twelve Councilors chosen from the SOCIETY at large, and one representative from each local section for every one hundred members or fraction thereof, in good standing, residing within its territory.

In 1923 the Council, having grown unwieldy through its expansion to one hundred ninety-four members, passed a By-Law establishing an Executive Committee to act ad interim for and on behalf of the Council on all matters of national policy or import and to serve in an advisory capacity in connection with matters coming before the Council. The Executive Committee has been very helpful, especially in arranging matters in concise form to be brought before the Council, thereby avoiding unnecessary discussion and expediting business.

CONSTITUTION AND BY-LAWS.—The Constitution and By-Laws of the SOCIETY have undergone changes from time to time as necessity arose with the growth of the SOCIETY and with the changed conditions in the country. Under its wise provisions the SOCIETY functions efficiently and every member of the SOCIETY has complete representation and equal opportunity in SOCIETY affairs. The Council meets twice a year, at the two general meetings of the SOCIETY, and may be called into session at any time by the President.

COMMITTEES.—The business of the SOCIETY is conducted quite largely through committees, which change frequently and automatically retire, unless reappointed by the President, at the time of the spring meeting. In order that the members may have full

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[1] For officers, 1876–1901, see *J Am Chem. Soc*, Supplement (Twenty-fifth Anniversary of the American Chemical Society), p. 79 (1902).

information in regard to the officers and the committees, they are regularly printed in each issue of the *Journal of the American Chemical Society.*

LOCAL SECTIONS.—The local sections of the SOCIETY have grown in number from the establishment of the Rhode Island Section in 1891 until there are seventy sections in active operation throughout the United States. They are given territory within which the members may be reasonably expected to attend the meetings at the sectional headquarters, and all members of the SOCIETY residing within that territory are *ipso facto* members of the local section. The local sections meet at stated times, determined by each section, usually monthly, from September until June. They have their own programs, conduct their own business, and are essentially autonomous in local affairs. No local section can commit the SOCIETY in any matter of national scope. Each local section receives from the general SOCIETY an amount varying from seventy-five cents to one dollar and fifty cents per member in reverse proportion to the number of their members. They may make rules and regulations for their government not inconsistent with the Constitution and By-Laws of the SOCIETY. They each have definite headquarters, both headquarters and territory being subject to the approval of the Council, which may change them if desirable.

Following is a list of the local sections arranged in the order of their establishment:

Local Sections
(In order of establishment)

NAME	DATE CHARTERED	HEADQUARTERS	MEMBERSHIP
Rhode Island	January 21, 1891	Providence, R. I.	92
New York	September 30, 1891	New York, N. Y.	1255
Cincinnati	March 29, 1892	Cincinnati, Ohio	221
Washington, D. C.	April 13, 1893	Washington, D. C.	389
Lehigh Valley	December 8, 1893	Easton and Bethlehem, Pa.	93
New Orleans	August 5, 1894	New Orleans, La.	*
Chicago	May 10, 1895	Chicago, Ill.	809
Nebraska	May 10, 1896	Lincoln, Nebr.	26
North Carolina	December 6, 1896	Raleigh, N. C.	57
Columbus	October 7, 1897	Columbus, Ohio	105
Northeastern	March 7, 1898	Boston, Mass.	775
Philadelphia	April 15, 1899	Philadelphia, Pa.	609
University of Michigan	December 7, 1899	Ann Arbor, Mich.	70
Kansas City	November 6, 1900	Kansas City, Mo.	146
California	December 31, 1901	San Francisco, Calif.	350
Cornell	December 9, 1902	Ithaca, N. Y.	58
Pittsburgh	February 11, 1903	Pittsburgh, Pa.	397
Georgia	January 23, 1904	Atlanta, Ga.	45
Iowa	March 27, 1905	Iowa City, Iowa	105
Western New York	November 18, 1905	Buffalo, N. Y.	243
Minnesota	January 4, 1906	Minneapolis, Minn.	186

Local Sections (*Concluded*)
(In order of establishment)

NAME	DATE CHARTERED	HEADQUARTERS	MEMBERSHIP
Indiana	February 2, 1906	Indianapolis, Ind.	137
University of Illinois	April 9, 1906	Urbana, Ill.	139
Louisiana	June 28, 1906	New Orleans, La.	76
Syracuse	May 6, 1907	Syracuse, N. Y.	103
Wisconsin	July 9, 1907	Madison, Wis.	120
St. Louis	July 26, 1907	St Louis, Mo.	202
Eastern New York	January 7, 1908	Schenectady, N. Y	104
Louisville	July 18, 1908	Louisville, Ky.	27
Milwaukee	December 8, 1908	Milwaukee, Wis	115
Cleveland	January 6, 1909	Cleveland, Ohio	240
Puget Sound	February 16, 1909	Seattle, Wash.	65
University of Missouri	June 3, 1909	Columbia, Mo.	31
Nashville	January 5, 1911	Nashville, Tenn.	23
Southern California	February 28, 1911	Los Angeles, Calif	288
Connecticut Valley	April 12, 1911	Hartford, Conn.	110
Detroit	January 3, 1912	Detroit, Mich	143
New Haven	February 3, 1912	New Haven, Conn.	107
Northern Inter-Mountain	April 4, 1912	Pullman, Wash.	*
Lexington	April 24, 1912	Lexington, Ky.	30
Maine	April 24, 1912	Orono, Me.	35
Oregon	July 5, 1912	Portland, Ore.	44
Rochester	July 5, 1912	Rochester, N. Y.	139
Alabama	March 24, 1913	Birmingham, Ala.	37
South Carolina	April 14, 1914	Columbia, S. C.	*
Maryland	September 23, 1914	Baltimore, Md.	217
Virginia	April 9, 1915	Richmond, Va.	96
Ames	October 12, 1915	Ames, Iowa	55
South Dakota	April 29, 1916	Vermillion, S. D.	*
Vermont	April 29, 1916	Burlington, Vt.	23
Central Texas	April 18, 1917	College Station, Tex.	52
Michigan State College	April 18, 1917	East Lansing, Mich.	36
Southeastern Texas	April 18, 1917	Port Arthur, Tex.	81
Toledo	April 18, 1917	Toledo, Ohio	40
Delaware	December 28, 1917	Wilmington, Del.	160
Oklahoma	May 14, 1919	Stillwater, Okla.	74
Midland	December 8, 1919	Midland, Mich.	23
Colorado	April 21, 1920	Denver, Colo.	71
South Jersey	April 21, 1920	Carneys Point, N. J.	31
Omaha	May 6, 1920	Omaha, Nebr.	34
Savannah	May 10, 1920	Savannah, Ga.	*
Arkansas	May 7, 1921	Fayetteville, Ark.	*
Purdue	January 3, 1922	Lafayette, Ind.	23
St. Joseph Valley	January 3, 1922	South Bend, Ind.	22
Hawaiian	April 21, 1922	Honolulu, T. H.	29
Sacramento	April 21, 1922	Sacramento, Calif.	27
Northern West Virginia	April 28, 1922	Morgantown, W. Va.	26
Akron	March 5, 1923	Akron, Ohio	138
Erie	April 9, 1923	Erie, Pa.	36
Illinois-Iowa	July 20, 1923	Davenport, Iowa	26
Florida	January 4, 1924	Gainesville, Fla.	54
Central Pennsylvania	February 7, 1924	State College, Pa.	56
Arizona	April 29, 1924	Tucson, Ariz	23
Northwestern Utah	April 29, 1924	Salt Lake City, Utah	27
North Jersey	July 22, 1925	Newark, N. J.	542
Northern Louisiana	November 30, 1925	Shreveport, La.	24

* Discontinued.

DIVISIONS.—In the chemical life of all countries there are two interests, "useless each without the other," but for some unexplainable reason always more or less at variance. In no country but our own have the pure and applied chemical scientists been able to work together in one organization with mutual appreciation and without serious jealousies. This is one of the chief secrets of the success of the AMERICAN CHEMICAL SOCIETY, which was brought about through the wise foresight of President Bogert, who, in 1909, clearly foresaw that the SOCIETY was likely to disintegrate unless some method was devised by which specialists in various branches of chemistry might gather together in essentially autonomous meetings. Accordingly, he inaugurated the divisional system, establishing first the Division of Industrial and Engineering Chemistry, followed gradually by others, until now the SOCIETY conducts its activities in seventeen divisions and two sections. Sections differ little from divisions except that they are not given divisional status with by-laws and officers of their own until they have held a sufficient number of meetings to prove the need and demand for their special services. The divisions are professional groups organized from members of the SOCIETY and authorized by the Council to stimulate and develop the growth of the special activity assigned to them. They elect their own officers; they have the right to make by-laws for their own government, subject to the approval of the Council and not inconsistent with the Constitution and By-Laws of the SOCIETY; they may collect funds to be expended for their own purposes, and have the entire control and management of such funds. Their chairmen are Vice Presidents of the SOCIETY and ex officiis members of the Council.

The divisions have proved of the utmost benefit to the AMERICAN CHEMICAL SOCIETY and its growth. Through them the need of the specialist is met. Each division has every advantage which can come to an entirely separate organization and enjoys likewise the great additional advantage which comes with union and strength of numbers. In a sense, then, the SOCIETY is constituted in much the same way as our national Government—the divisions represent the states, functioning quite as independently and conducting their specialized affairs and programs with almost complete autonomy. No wiser step has been taken in the SOCIETY's development than the organization of the divisional system. *Industrial and Engineering Chemistry* was established shortly after the organization of the Division of Industrial and Engineering Chemistry, and it became the journal especially assigned to the branches which its name implies, more particularly with reference to research.

The divisions of the SOCIETY, alphabetically arranged, with date of their authorization and their officers, are as follows:

Divisions of the American Chemical Society

AGRICULTURAL AND FOOD CHEMISTRY.—*Authorized,* 1908. *Chairmen:* W. D. Bigelow, 1909; C. D. Woods, 1910; H. E. Barnard, 1911–13; Floyd W. Robison, 1914–15; L. M. Tolman, 1916; T. J. Bryan, 1917–18; W D. Richardson, 1919; C. E. Coates, 1920–21; T. J. Bryan, 1922; H. A Noyes, 1923; C. H. Bailey, 1924–25; E. F. Kohman, 1926. *Secretaries:* W. B D. Penniman, 1909; B. E. Curry, 1910–11; Glen F. Mason, 1912–15; George B. Taylor, 1916; Glen F. Mason, 1917; Fred F. Flanders, 1918; T. J. Bryan, 1919–21; C. S Brinton, 1922– .

BIOLOGICAL CHEMISTRY.—*Authorized,* 1913. *Chairmen:* C. L. Alsberg, 1914–17; W. J. N. Osterhout, 1918; I. K. Phelps, 1919; R. A. Gortner, 1920, A. W. Dox, 1921; H. B. Lewis, 1922; J. S Hughes, 1923; W. T. Bovie, 1924, R. Adams Dutcher, 1925; R. J. Anderson, 1926 *Secretaries:* I. K. Phelps, 1914–18; R. A. Gortner, 1919; A. W. Dox, 1920; H. B. Lewis, 1921; J. S. Hughes, 1922; W. T. Bovie, 1923; R. Adams Dutcher, 1924; R. J. Anderson, 1925; J. J. Willaman, 1926.

CELLULOSE CHEMISTRY.—*Authorized,* 1922. *Chairmen:* G. J. Esselen, Jr., 1923–24; H. LeB. Gray, 1925– . *Secretary:* L. F. Hawley, 1923– .

CHEMICAL EDUCATION.—*Authorized,* 1924. *Chairmen:* W. A. Noyes, 1925; Wilhelm Segerblom, 1926. *Secretary:* B. S. Hopkins, 1925– .

DYE CHEMISTRY.—*Authorized,* 1920. *Chairmen:* A. B. Davis, 1920–21; W. J. Hale, 1922–24; R. Norris Shreve, 1925– . *Secretaries:* R. Norris Shreve, 1920–24; O. E. Roberts, Jr., 1925– .

FERTILIZER CHEMISTRY.—*Authorized,* 1908. *Chairmen:* F. B Carpenter, 1909–10; Paul Rudnick, 1911–13; J. E. Breckenridge, 1914–18; F. B Carpenter, 1919– . *Secretaries:* J. E. Breckenridge, 1909–10; J. P. Street, 1911–12; J. E. Breckenridge, 1913; E. L. Baker, 1914–15; F. B. Carpenter, 1916; L. L. Van Slyke, 1917; F. B. Carpenter, 1918; H. C. Moore, 1919–

GAS AND FUEL CHEMISTRY.—*Authorized,* 1925. *Chairmen:* R T. Haslam, 1925; S. W. Parr, 1926. *Secretary:* O. O. Malleis, 1925– .

INDUSTRIAL AND ENGINEERING CHEMISTRY.—*Authorized,* 1908. *Chairmen:* A. D. Little, 1908–10; G. C. Stone, 1911; George D. Rosengarten, 1912–15; H. E. Howe, 1916–17; H. S. Miner, 1918–19; H. D. Batchelor, 1920–21; W. K. Lewis, 1922; D. R. Sperry, 1923–24; W. A. Peters, Jr., 1925– . *Secretaries:* B. T. B. Hyde, 1908–9; G. C. Stone, 1910; F. E. Gallagher, 1911; Geo. P. Adamson, 1912; S. H. Salisbury, 1913; H. E. Howe, 1914–15; S. H. Salisbury, 1916–18; H. E. Howe, 1919–21; E. M. Billings, 1922– .

LEATHER AND GELATIN CHEMISTRY.—*Authorized,* 1921. *Chairman:* J. Arthur Wilson, 1922– . *Secretary:* Arthur W. Thomas, 1922– .

MEDICINAL PRODUCTS, CHEMISTRY OF.—*Authorized,* 1909. *Chairmen:* A. B. Stevens, 1910; B. L. Murray, 1911–13; Frank R. Eldred, 1914–15; J. H. Long, 1916; L. F. Kebler, 1917; F O. Taylor, 1918–19; Charles E. Caspari, 1920–21; Edgar B. Carter, 1922–23; E. H. Volwiler, 1924–25; H. A. Shonle, 1926. *Secretaries:* B. L. Murray, 1910; Frank R. Eldred, 1911–13; L. A. Brown, 1914–15; George D. Beal, 1916–19; Edgar B. Carter, 1920–21; E. H. Volwiler, 1922–23; H. A. Shonle, 1924–25; Arthur W. Dox, 1926.

ORGANIC CHEMISTRY.—*Authorized,* 1909. *Chairmen:* E. C. Franklin, 1910; G. B. Frankforter, 1911; Treat B. Johnson, 1912–13; B. F. Allen, 1914–15; C. G. Derick, 1916; J. R. Bailey, 1917; William J. Hale, 1918; L. W. Jones, 1919; E. E Reid, 1920; Roger Adams, 1921; H. T. Clarke, 1922; Frank C. Whitmore, 1923; R. R Renshaw, 1924; J. A. Nieuwland, 1925; Marston T. Bogert, 1926. *Secretaries:* R. H. McKee, 1910; William J. Hale, 1911–13; C. G. Derick, 1914–15; Harry L. Fisher, 1916–19; Roger Adams, 1920; H. T. Clarke, 1921; Frank C. Whitmore, 1922; R. R. Renshaw, 1923; J. A. Nieuwland, 1924; Frank C. Whitmore, 1925– .

PETROLEUM CHEMISTRY.—*Authorized,* 1922. *Chairman:* R. R. Matthews, 1923– . *Secretaries:* W. A. Gruse, 1923; G. A. Burrell, 1924– .

PHYSICAL AND INORGANIC CHEMISTRY.—*Authorized*, 1908. *Chairmen:* Charles H. Herty, 1909; E. C. Franklin, 1910; H. P. Talbot, 1911; W. Lash Miller, 1912; S. L. Bigelow, 1913; G. A. Hulett, 1914–15; E. W. Washburn, 1916; T. W. Richards, 1917; S. L. Bigelow, 1918; W. E. Henderson, 1919; W. D. Harkins, 1920; Harry N. Holmes, 1921; S. E. Sheppard, 1922; Robert E. Wilson, 1923; Graham Edgar, 1924; Arthur Hill, 1925; H. B. Weiser, 1926. *Secretaries:* W. D. Bancroft, 1909; S. L. Bigelow, 1910–11; Roger C. Wells, 1912–13; H. N. McCoy, 1914–15; James Kendall, 1916; Earl B. Millard, 1917; W. E. Henderson, 1918; W. A. Patrick, 1919; Harry N. Holmes, 1920; S. E. Sheppard, 1921; Robert E. Wilson, 1922; Graham Edgar, 1923; H. B. Weiser, 1924; G. S. Forbes, 1925; G. L. Clark, 1926.

RUBBER CHEMISTRY.—*Authorized*, 1919. *Chairmen:* J. B. Tuttle, 1919; W. K. Lewis, 1920; W. W. Evans, 1921; C. W. Bedford, 1922; W. B. Wiegand, 1923; E. P. Spear, 1924; C. R. Boggs, 1925; J. M. Bierer, 1926. *Secretary:* Arnold H. Smith, 1919– .

SUGAR CHEMISTRY.—*Authorized*, 1921. *Chairmen:* S. J. Osborn, 1922; W. D. Horne, 1923; F. W. Zerban, 1924; W. B. Newkirk, 1925– . *Secretary:* Frederick J. Bates, 1922– .

WATER, SEWAGE, AND SANITATION CHEMISTRY.—*Authorized*, 1915. *Chairmen:* Edward Bartow, 1915–16; R. B. Dole, 1917; R. S. Weston, 1918–19; J. W. Ellms, 1920; W. P. Mason, 1921; A. M. Buswell, 1922–23; W. W. Skinner, 1924; F. W. Mohlman, 1925– . *Secretaries:* H. P. Corson, 1915–16; E. H. S. Bailey, 1917; Frank E. Hall, 1918; W. W. Skinner, 1919–23; F. R. Georgia, 1924–

In addition to the above-mentioned divisions, the Section of the History of Chemistry and the Section of Paint and Varnish Chemistry have been operating successfully through a number of meetings with every prospect of being soon given divisional status.

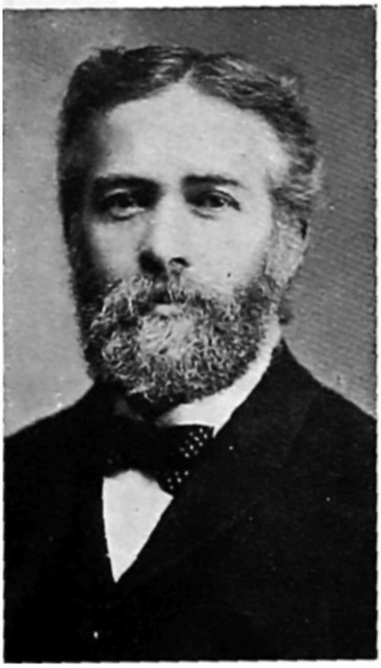
MEETINGS.—The AMERICAN CHEMICAL SOCIETY holds two meetings a year, in the spring and in the fall, usually in April and in September. At these conventions from 400 to 2500 chemists gather to conduct the business of the SOCIETY, to meet and form contacts with one another, and to present or listen to scientific programs, both general and divisional. The meetings are held in different parts of the United States or Canada on invitation, usually from one of the SOCIETY'S local sections, and with the special idea of stimulating chemical interest and development in the region visited.

The general meetings held by the AMERICAN CHEMICAL SOCIETY since the first general meeting in Newport, Rhode Island, in August, 1890, are as follows:

General Meetings of the American Chemical Society

1. Newport, R. I., August 6–7, 1890.
2. Philadelphia, Pa., December 30–31, 1890.
3. Washington, D. C , August 17–18, 1891.
4. New York, N. Y., December 29–30, 1891.
5. Rochester, N. Y., August 16–17, 1892.
6. Pittsburgh, Pa., December 28–29, 1892.
7. Chicago, Ill., August 21–22, 1893.
8. Baltimore, Md., December 17–18, 1893.
9. Brooklyn, N. Y., August 15–16, 1894.
10. Boston and Cambridge, Mass., Dec. 27–28, 1894.

11. Springfield, Mass., August 27–28, 1895.
12. Cleveland, Ohio, December 30–31, 1895.
13. Buffalo, N. Y., August 21–22, 1896.
14. Troy, N. Y., December 29–30, 1896.
15. Detroit, Mich., August 9–10, 1897.
16. Washington, D. C., December 29–30, 1897.
17. Boston, Mass., August 22–23, 1898.
18. New York, N. Y., December 28–29, 1898.
19. Columbus, Ohio, August 21–22, 1899.
20. New Haven, Conn., December 27–28, 1899.
21. New York, N. Y., June 25–26, 1900.
22. Chicago, Ill., December 27–28, 1900.
23. New York, N. Y., April 12–13, 1901.
24. Denver, Colo., August 26–27, 1901.
25. Philadelphia, Pa., December 30–31, 1901.
26. Pittsburgh, Pa., June 30–July 1, 1902.
27. Washington, D. C., December 29–30, 1902.
28. Cleveland, Ohio, June 29–30, 1903.
29. St. Louis, Mo., December 30–31, 1903.
30. Providence, R. I., June 21–23, 1904.
31. Philadelphia, Pa., December 30–31, 1904.
32. Buffalo, N. Y., June 22–24, 1905.
33. New Orleans, La., December 29–30, 1905.
34. Ithaca, N. Y., June 28–30, 1906.
35. New York, N. Y., December 27–30, 1906.
36. Toronto, Canada, June 27–29, 1907.
37. Chicago, Ill., December 31, 1907–January 3, 1908.
38. New Haven, Conn., June 29–July 2, 1908.
39. Baltimore, Md., December 29, 1908–January 1, 1909.
40. Detroit, Mich., June 29–July 2, 1909.
41. Boston, Mass., December 27–31, 1909.
42. San Francisco, Calif., July 12–16, 1910.
43. Minneapolis, Minn., December 28–31, 1910.
44. Indianapolis, Ind., June 28–July 1, 1911.
45. Washington, D. C., December 27–30, 1911.
46. New York, N. Y., September 11, 1912.
47. Milwaukee, Wis., March 25–28, 1913.
48. Rochester, N. Y., September 8–12, 1913.
49. Cincinnati, Ohio, April 6–10, 1914.
50. New Orleans, La., March 31–April 3, 1915.
51. Seattle, Wash., August 31–September 3, 1915.
52. Urbana-Champaign, Ill., April 18–21, 1916.
53. New York, N. Y., September 25–30, 1916.
54. Kansas City, Mo., April 10–13, 1917.
55. Boston, Mass., September 9–13, 1917.
56. Cleveland, Ohio, September 10–13, 1918.
57. Buffalo, N. Y., April 7–11, 1919.
58. Philadelphia, Pa., September 2–6, 1919.
59. St. Louis, Mo., April 12–17, 1920.
60. Chicago, Ill., September 6–10, 1920.
61. Rochester, N. Y., April 25–30, 1921.
62. New York, N. Y., September 6–10, 1921.
63. Birmingham, Ala., April 3–7, 1922.
64. Pittsburgh, Pa., September 4–8, 1922.
65. New Haven, Conn., April 2–7, 1923.
66. Milwaukee, Wis., September 10–14, 1923.
67. Washington, D. C., April 21–26, 1924.
68. Ithaca, N. Y., September 10–13, 1924.
69. Baltimore, Md., April 6–10, 1925.
70. Los Angeles, Calif., August 3–8, 1925.
71. Tulsa, Okla , April 5–9, 1926.
72. Philadelphia, Pa., September 6–11, 1926.



George C. Caldwell
(1834–1907)
President 1892

Underwood & Underwood

Harvey W. Wiley
(1844–   )
President 1893, 1894

Edgar F. Smith
(1854–   )
President 1895, 1921, 1922

Charles B. Dudley
(1842–1909)
President 1896, 1897

The SOCIETY has grown so large that the meetings of the local sections and the general meetings of the SOCIETY have of late not entirely satisfied the demands of all its members. Accordingly, two additional forms of chemical meetings have recently become popular:

First, regional or intersectional meetings, in which at various times, without interfering with the general meetings of the SOCIETY, groups of local sections convene for one or two days on their own initiative, through their own organizations, and by mutual agreement. Chemists who take part in these regional meetings gather for purposes of good fellowship, making new acquaintances, the presentation of scientific papers, and the discussion of common problems.

Second, special divisional meetings or symposia by groups of specialists. This form of meeting has recently come into vogue and unquestionably meets a pressing demand of the specialist. They are quite frequently joined with, and made the chief feature of, one of the regional or intersectional meetings. For example, the organic chemists of the country, with the full approval of the general SOCIETY, held a symposium on organic chemistry with the Rochester Section, December 29–31, 1925. The program was one of the most successful organic chemical programs ever presented in the United States and the leading organic chemists of America were present. A little later, February 22–23, 1926, the Division of Rubber Chemistry held a separate program upon the problems of rubber chemistry in the center of the rubber industry, and with the local section of the AMERICAN CHEMICAL SOCIETY at Akron. Some three hundred and fifty chemists interested in the chemistry of India rubber were present, and thus another separate divisional meeting was held within the SOCIETY which satisfied fully the legitimate desires of these chemists to convene and discuss their specialty.

Likewise, the Section of Paint and Varnish Chemistry, soon destined to become a division of the AMERICAN CHEMICAL SOCIETY, met for a special program in their field with the Wisconsin Section at Madison, May 27–29, 1926. The leading chemists in the paint and varnish industry were present, and an enthusiastic meeting was again the result.

All of these special meetings were held after consultation with the officers of the SOCIETY, in order not to transgress but to supplement and extend the aims and objects of the SOCIETY's general meetings.

Some members have felt that these separate meetings would tend to a division of the SOCIETY into smaller associations. Such, however, is far from being the case. On the contrary, they serve to bind the SOCIETY more closely together. They meet the demand of the specialist and, being within the SOCIETY, their members share the strength and common purpose that come from the union of all American chemists in one great organization which, serving one and all alike, can furnish them with the printed record of chemical research and development throughout the world. The attending chemists went from each one of these separate divisional meetings more loyal members of the AMERICAN CHEMICAL SOCIETY, for they realized more fully than ever before that the sole object of the AMERICAN CHEMICAL SOCIETY is the advancement of chemistry, the development of chemical research, and the welfare of American chemists.

LIBRARY.—The library of the AMERICAN CHEMICAL SOCIETY, which has been gradually growing through its fifty years of existence, has been made a part of the library of the Chemists Club of New York City. All members of the AMERICAN CHEMICAL SOCIETY have access to the combined library, but the library personnel and space are furnished by the Chemists Club. This arrangement was made with the Chemists Club in 1912.

NEWS SERVICE.—When chemistry began to arouse the interest of the newspaper editors of the country, it became evident that the SOCIETY must either take steps to provide authentic information, prepared in a form attractive to the daily press, or else chemistry would suffer from the inclination to overemphasize the sensational development in the science. Following the advice of a committee appointed to study publicity, the Directors in 1917 provided five hundred dollars with which to begin this activity. No record of results was kept for that year, but clippings were measured from 1918 until 1924, inclusive, when the number became too great to warrant the cost of collection. Results are shown in the following table:

American Chemical Society News Service Clippings

YEAR	COST	INCHES
1917	$ 500	——
1918	1,850	5,000
1919	2,069	8,000
1920	8,078	21,000
1921	12,792	70,000
1922	10,306	79,000
1923	8,154	115,000
1924	6,580	205,000
1925	7,758	——

The gain in publicity indicates both the need and the success of the AMERICAN CHEMICAL SOCIETY News Service. The releases have been given prominence in the most important daily papers, magazines, and trade publications, both at home and abroad. Tangible results of benefit to chemistry can be recorded to the credit of the News Service, and the SOCIETY's success has been envied by other scientific organizations. The News Service stands as a national institution accredited by the press and used in increasing measure by editors who realize the interest of their readers in the subject and who desire to present, in authentic form, news of the latest advances of our science.

PRIZE ESSAY CONTESTS.—Convinced of the necessity for developing an intelligent appreciation of the vital relation of chemistry to national progress, safety, and public welfare, Hon. and Mrs. Francis P. Garvan offered a series of prizes in 1923 to be awarded to students in high and secondary schools, both public and private, on a basis which made it possible to give six first prizes in each state of the Union and six national prizes. The state prizes were twenty dollars each, while each national winner received a four-year college scholarship, plus five hundred dollars annually for four years. This magnanimous offer was followed by the announcement that ways had been found for distributing a set of five books as the nucleus of a library which could be read with interest and understanding by non-technically trained people. Many sets of these books were distributed to schools and libraries without cost, and others were offered at the nominal price of two dollars and a half per set.

The books distributed were:

"Creative Chemistry," by Edwin E. Slosson
"Life of Pasteur," by René Vallery-Radot
"Riddle of the Rhine," by Victor Lefebure
"Discovery, or The Spirit and Service of Science," by Sir Richard Gregory
"The Future Independence and Progress of American Medicine in the Age of Chemistry," by a Committee of American Scientists.

The subjects chosen for the essays were:

The Relation of Chemistry to Health and Disease
The Relation of Chemistry to the Enrichment of Life
The Relation of Chemistry to Agriculture or Forestry
The Relation of Chemistry to National Defense
The Relation of Chemistry to the Home
The Relation of Chemistry to the Development of an Industry or a Resource of the United States.

A national committee was organized with Hon. Herbert Hoover as chairman. Thanks to the interest and assistance of members of the SOCIETY and many business and professional men and women interested in the objects of the contest, as well as school officials and teachers, this contest was successful from the start and has been succeeded by a similar contest each year. Notwithstanding the large number of national contests, this series, under the auspices of the SOCIETY, has been recognized for its inherent merit and continues to receive gratifying support.

In 1924 a contest was added for the best essays in the same subjects among college students, the prizes being six in number, of one thousand dollars each. This contest was repeated in the academic year of 1925–1926 and is to be held again in 1926–1927, but will be limited to members of the freshman class. In 1926–1927 there will also be a contest on the same subjects with cash prizes open to students in normal schools and teachers' colleges.

Following the distribution of the first set of books, there have been provided two volumes of "Chemistry in Industry" and one of "Chemistry in Agriculture" to meet the need for books in these subjects. These books have been prepared by specialists and are written in non-technical language so as to be easily understood by the contestants. Some fifty thousand of the original sets of books have been distributed and a like number of volumes of "Chemistry in Industry."

It is believed that this activity is one of utmost importance to the future of chemistry in America. Its purpose is not to increase the number of those who make chemistry their profession, but rather to create a growing public interest in chemistry and chemical activity and to encourage the acquisition of knowledge about chemistry, as distinguished from a study of the science from the professional point of view. The generous and increasing support that has come to chemistry in America may be traced in no small degree to the influence of the Prize Essay Contest and to the efforts of those who, through the contest, have come to appreciate what chemistry means.

MEDALS.—Three medals have been established by the AMERICAN CHEMICAL SOCIETY, or by its local sections.

The Priestley Medal.—The Priestley Medal was founded by the AMERICAN CHEMICAL SOCIETY from the residue of a fund collected by the Priestley Memorial Committee for the purpose of placing a portrait of Joseph Priestley, the discoverer of oxygen, in the National Museum at Washington, D. C.

The Priestley Medal is an award of the general SOCIETY and is given every three years for distinguished services to chemistry. It may be awarded to a citizen of any nation without regard to sex. The recipient may be invited to deliver an address at one of the general meetings of the AMERICAN CHEMICAL SOCIETY. The medal has been awarded as follows:

1923—Ira Remsen, no address.
1926—Edgar F. Smith, "Joseph Priestley."

The Nichols Medal.—This medal was established by William H. Nichols in New York in 1902 to stimulate original research in chemistry. It is presented annually, provided, in the opinion of the jury of award, there is a worthy recipient. It is open to investigators who have published original contributions in any of the journals of the AMERICAN CHEMICAL SOCIETY, or of those published under its auspices, during the three calendar years next preceding the presentation meeting. It is presented at the March meeting of the New York Section of the AMERICAN CHEMICAL SOCIETY, and the recipient is expected at that time to deliver an address upon the subject of the award. The following have been awarded the Nichols Medal:

Recipients of the Nichols Medal

YEAR	RECIPIENT	TITLE OF RESEARCH
1903	E. B. Voorhees	Studies in Denitrification
1904	No award	
1905	Charles L. Parsons	Atomic Weight of Beryllium
1906	Marston T. Bogert	Researches on Quinazolines
1907	M. B. Bishop	Estimation of Arsenic
1908	W. H. Walker	Corrosion of Iron
1909	W. A. Noyes H. C. P. Weber	Atomic Weight of Chlorine
1910	L. H. Baekeland	Researches on Bakelite
1911	M. A. Rosanoff C. W. Easley	On the Partial Vapor Pressure of Binary Mixtures
1912	Charles James	Rare Earth Compounds
1913	No award	
1914	Moses Gomberg	Triphenylmethyl
1915	Irving Langmuir	Chemical Reactions at Low Pressures
1916	Claude S. Hudson	Researches on Sugars
1917	No award	
1918	Treat B. Johnson	Researches on Pyrimidines
1919	No award	
1920	Irving Langmuir	Arrangements of Electrons in Atoms and Molecules
1921	Gilbert N Lewis	The Third Law of Thermodynamics
1922	No award	
1923	Thomas Midgely, Jr.	Some Fundamental Relations among the Elements as Regards the Suppression of Gaseous Detonation
1924	Charles A. Kraus	The Properties of Non-Aqueous Solutions
1925	E. C. Franklin	The Ammonia System of Compounds
1926	Samuel C. Lind	Chemical Activation by Alpha Particles

Willard Gibbs Medal.—The Willard Gibbs Medal, founded by William A. Converse in 1910, is awarded annually by the Chicago Section of the AMERICAN CHEMICAL SOCIETY to anyone who, on account of his eminent work in any original contributions to pure and applied chemistry, is deemed worthy of special recognition by the jury of award. A recipient of the medal is expected to give an address upon a chemical subject of his own selection and satisfactory to the jury of award at a meeting of the Chicago Section. The recipients have been as follows:

Recipients of the Willard Gibbs Medal

YEAR	RECIPIENT	TITLE OF RESEARCH
1911	Svante Arrhenius	Electrolytic Dissociation
1912	Theodore W. Richards	Atomic Weights
1913	Leo H. Baekeland	Recent Developments in Phenolic Condensation
1914	Ira Remsen	The Development of Chemical Research in America
1915	Arthur A. Noyes	A System of Qualitative Analysis Including Nearly All the Elements
1916	Willis R. Whitney	Incidents of Applied Research
1917	Edward W. Morley	Early Researches in Hydrogen and Oxygen
1918	Wm. M. Burton	Chemistry in the Petroleum Industry
1919	Wm. A. Noyes	Positive and Negative Valences
1920	F. G. Cottrell	International Scientific Relations
1921	Marie Sklodowska Curie	The Discovery of Radium
1922	No award	
1923	Julius Stieglitz	Theory of Color Production in Dyes
1924	Gilbert N. Lewis	The Molecule as a Magnet
1925	Moses Gomberg	Elements with Abnormal Valence
1926	James C. Irvine	

Finances[1]

The AMERICAN CHEMICAL SOCIETY has been financed almost wholly by American chemists themselves. Membership dues at first were five dollars per member. A little later they were made ten dollars for resident members in New York and five dollars for non-resident members. Subsequently, they were reduced again to five dollars for all members and were maintained at this figure until 1907, when *Chemical Abstracts* was established and the dues were increased to eight dollars. In 1909, with the establishment of the *Journal of Industrial and Engineering Chemistry,* the dues were changed to ten dollars and were continued at this amount until 1921, when increased costs of publication necessitated an additional increase to fifteen dollars.

It has been a fundamental principle of the SOCIETY from the beginning that every member should pay equal dues and be entitled to all of the publications of the general SOCIETY. On this basis the SOCIETY has prospered, and only on this basis

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[1] For a full discussion of the SOCIETY's business management and expenditures see *Ind. Eng. Chem.*, News Edition, January 20, 1923.

could the publication of its journals be financed. There is no reduction in dues to the member who wishes to give up one or more of the three journals to which he is entitled. This is because the item of "putting on the press" is by far the largest item of publication. This expense is the same whether one or fifteen thousand copies are printed. It is only because the Society has so many members that it can offer all three of its journals at a less cost than the price charged for many single journals of smaller size published abroad, where the actual expenses of printing are lower. Accordingly, since all members join in the cost of publication of all three journals and can receive all three if they desire, the overhead for each is decreased. The American Chemical Society has been able to give to its members chemical literature of the highest quality at a cost approximately one-half of that of like journals in any foreign country.

The increase of dues in 1921 came at a very unfortunate time for the Society, although necessary on account of the increased costs of labor and of paper. It happened to come during our greatest recent industrial depression and at a time when many chemists were thrown out of employment. The Society had its largest membership in 1920 when the country was unusually prosperous, when all chemists were fully employed, and when dues were only ten dollars a year. The increase to fifteen dollars a year has, however, given the Society a greater income and has enabled it to continue its publication of the rapidly increasing volume of chemical research.

In 1922 the income of the Society was not sufficient to meet the estimated budget of its officers, and the Directors felt it necessary to consider a decrease in the allotment of each one of the journals by ten per cent. In this emergency, the Chemical Foundation voluntarily came forward with a donation of twenty-five thousand dollars, and the severe retrenchment was accordingly avoided.

As elsewhere stated, the Chemical Foundation has also guaranteed the publication of the *Journal of Chemical Education* and the *Journal of Physical Chemistry*. In every way this organization has always proved itself a liberal friend of the American Chemical Society and has shown its desire to aid the work and aims of our organization.

At the end of its fifty years, the American Chemical Society has an annual expenditure of $340,000, of which approximately 85 per cent is for the publication of chemical literature. This $340,000 comes from the following sources:

Membership dues	$190,000
Non-member subscriptions	26,000
Sale of back numbers of its periodicals	5,000
Sale of reprints	3,000
Advertising[1]	105,000
Interest	6,000
Payments of foreign postage	5,000

Notwithstanding this large expenditure, the Society is finding no little difficulty in meeting the expense of adequately recording the results of chemical research in America. In other words, the volume of such research is increasing more rapidly than the income of the Society. As the publication of this research is only a fraction of one per cent of its material cost, the Society is making all possible efforts to obtain the necessary funds to insure the carefully edited publication of all worthy material. Among these efforts is an organized movement to obtain for its journals an endowment fund which shall relieve this pressure. Another increase of dues has been contemplated, but it is the judgment of those best informed that to increase the membership dues would in all probability decrease the Society's income.

The report of the Finance Committee, dated March 27, 1926,[2] shows that the principal amounts of the various funds of the Society stand as follows:

Morris Loeb Fund ($25,922.25).—This fund was established by a $25,000 bequest of Morris Loeb to the American Chemical Society for the support of a chemical type museum. The income from this fund is paid annually to the National Museum in Washington, which has established the museum, and is carrying out the wishes of Dr. Loeb as indicated in his will.[3]

Life Membership Fund ($6,235.04).—This fund is derived from the payments for Life Membership. The income is used to pay the annual dues of the Life Members while living. Any remaining balance can be devoted by constitutional provision to research. Appropriations may be made annually from the unexpended income of this fund, but only for the purposes of chemical research.

Priestley Fund ($1,115.75).—A fund collected by the Priestley Medal Committee as a basis of the triennial Priestley Medal.

Endowment Fund ($29,000).—In 1924 it became so evident that the demand upon our publications for space to record the results of chemical research was increasing so much more rapidly than the income of the Society that it was decided to undertake

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[1] Almost wholly in *Industrial and Engineering Chemistry*.

[2] *J. Am. Chem. Soc.*, Proceedings, **48**, 32 (1926).

[3] *Ibid.*, **35**, 71 (1913).

the procurement of an Endowment Fund, the income of which was to be expended solely to help finance the publications of the SOCIETY. The work of the Endowment Committee is progressing, but is not yet well under way. It was deemed desirable first to secure donations from the members of the AMERICAN CHEMICAL SOCIETY, in order that the policy of self-support which the SOCIETY has always maintained may be continued in so far as is possible. Up to the present time subscriptions to the Endowment Fund have only been received from the SOCIETY's members whose income, for the most part, is limited to their monthly salaries. They have already shown their appreciation of the value of the SOCIETY's work by the support which they have contributed during five decades and the fruit of their labors is indicated by the results of their almost unaided efforts.

The time has come when the SOCIETY must seek assistance from those who have funds to donate or bequeath for worthy objects. The chemical industries of the country have been so extremely prosperous from the application of the results of chemical research that they will undoubtedly realize the need of this financial support. Surely the country cannot afford to allow worthy chemical advancements and discoveries to go unrecorded. It is the expectation of the SOCIETY that this, its greatest need, will shortly be satisfied by adequate financial support.

GENERAL FUND ($108,656.96).—This is the accumulated surplus of the SOCIETY during its fifty years of existence. It is held as a reserve fund against special need. The interest from the fund is used annually for the current expenses of the SOCIETY.

In addition to its definitely established funds, the SOCIETY has collected advance subscriptions of $66,000 towards publishing the Second Decennial Index to *Chemical Abstracts*, which is almost wholly invested in Liberty Bonds pending its use in 1927. Some $40,000 of this fund will be returned to the treasury toward establishing a revolving fund of $100,000 for printing future Decennial Indexes to *Chemical Abstracts*. Of this amount $35,000 was presented to the SOCIETY for this purpose in 1925 by the International Education Board and $2500 by the du Pont Co.

With the exception of the $25,000 given in 1922 by the Chemical Foundation, the above $35,000 presented by the International Education Board, and certain smaller donations for enabling the SOCIETY to publish the first Decennial Index to *Chemical Abstracts*, the AMERICAN CHEMICAL SOCIETY has been financed from the beginning by the undivided efforts of its members.

Bequests

The AMERICAN CHEMICAL SOCIETY is in a position to receive and administer bequests for any worthy object relating to the advancement of chemistry or chemical research. Two bequests, the Loeb Chemical Type Museum Bequest before mentioned, and the Elizabeth Blee Frasch Bequest, have already been announced. The latter bequest is for one million dollars made to the United States Trust Company for research in the field of agricultural chemistry. The income of the fund is to be allotted, upon the advice of the AMERICAN CHEMICAL SOCIETY, to one or more incorporated institutions in the United States which shall be selected for the purpose. The SOCIETY is also expected to advise every five years as to whether the grant to any particular institution shall be continued or whether the income shall be allotted to others. The SOCIETY has been confidentially informed of three other bequests from donors yet living. The SOCIETY is always ready, without compensation of any kind, to give its services to the administration of any such bequests for the country's development through the aid of chemistry.

War Service of Chemists[1]

It having become apparent early in 1917, through personal contact of the SOCIETY'S officers with European conditions, that the chemists of America were to play a prominent part in the impending war, coöperative arrangements were made with the Bureau of Mines to collate a census of America's chemical personnel. The progress of America's allies in the application of chemistry to offensive and defensive warfare had been greatly handicapped by casualties among some of their most prominent chemists before it was realized that chemical brain power was far more valuable than the physical strength of chemists in the trenches. Science was being used as it never had been used before, and the only means of combating this form of warfare was with scientific, especially chemical, weapons. Already France, England, and Canada had withdrawn all chemists remaining in the service for chemical duty at home.

A census of chemists was accordingly started in February, 1917, giving full data as to the member's age, place of birth, lineage, citizenship, chemical training, experience, etc., in order that the information might be available when needed. Accordingly, detailed information regarding some 17,000 chemists was available when America entered the World War.

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[1] *J. Ind Eng. Chem.*, **10**, **776** (**1918**), **11**, **413** and **921–24** (**1919**).

Already, in the early part of February, 1917, the President of the AMERICAN CHEMICAL SOCIETY had offered, without reservation, the services of the AMERICAN CHEMICAL SOCIETY and of all its members to President Wilson for any emergency that might arise. In June, 1917, a committee of the SOCIETY presented a report[1] on "War Service of Chemists" and "A Plan for the Impressment of Chemists and for the Preservation of the Supply of Chemists," in order that America might meet any demand for chemical information, chemical personnel, and chemical production. A large number of the chemists engaged in war work were obtained from the SOCIETY'S classified list. Practically all of the chemists who early entered the service in a commissioned capacity were obtained through the AMERICAN CHEMICAL SOCIETY, and even those who were later engaged were passed upon by the SOCIETY'S officers.

When the Bureau of Mines began its investigations on gas warfare the SOCIETY'S classified list was invaluable, and representatives from practically all of the Government bureaus and departments in Washington used it freely as their needs increased. The demand for chemists became so great that a little later, through the far-sighted assistance of Secretary Crowell, all chemists being drafted or inducted into the Army were withheld for chemical service. From the first, the chemical personnel in the Army and Navy and in the civilian bureaus was partly civilian and partly military. As the war progressed and men were taken from the Army and assigned to chemical duty the proportion of chemists in uniform naturally increased. The investigations of gas warfare, which had reached a high state of efficiency with over 700 chemists and 1100 helpers under the direction of the Bureau of Mines, coöperating with the chemical service of the Army, were later taken over by the newly formed Chemical Warfare Service in June, 1918, and a goodly portion of the chemists wore its uniform.

Throughout the war the AMERICAN CHEMICAL SOCIETY maintained an office in Washington for its Committee on War Service for Chemists. This office was continually consulted by the War and Navy Departments when in need of chemical personnel or chemical assistance.

It was a real event in the history of chemistry when, as a result of conferences held at the Bureau of Mines with officers of the Medical Corps, War College, General Staff, Navy and civilian chemists, the Chemical Service Section was established as a unit of the Army. This was the first recognition of chemistry as a separate branch

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[1] *J. Ind. Eng. Chem*., 9, 639 (1917).

of the military service of any country in any war. Later, the Chemical Service Section, all the gas research laboratories and personnel of the Bureau of Mines, and the plant and field operations of the Ordnance and Medical Departments pertaining to gas warfare were united under the new title of "Chemical Warfare Service." In recognition of its direct growth from the efforts of the AMERICAN CHEMICAL SOCIETY, the new Chemical Warfare Service adopted for its colors those of the AMERICAN CHEMICAL SOCIETY, cobalt blue and gold.

The influence of the AMERICAN CHEMICAL SOCIETY and its help to America in the war have been told in detail in many articles appearing in *Industrial and Engineering Chemistry*. They naturally need not be repeated here. It is perhaps quite sufficient to say that the American chemist fully met his obligations. The chemical program of the United States Army and Navy exceeded at all times the requirements of our trained man-power in the mechanical devices necessary to apply what the chemists of America had produced.

When the war closed there were, according to the SOCIETY's record, 4003 chemists in uniform serving in a chemical capacity. In addition, there was fully an equal number serving as civilians in laboratories supported by or under the auspices of the Government. The rest of the members of the AMERICAN CHEMICAL SOCIETY had remained through necessity in the country's chemical and munition plants by direction of the Government in order that these important supplies might not be lacking. All American chemists were in service.

The Secretary of War[1] in a public address stated:

> The AMERICAN CHEMICAL SOCIETY presented a striking instance of preparedness. It certainly had the largest body of its kind in the world and comprised in its ranks 14,500 of the 17,000 chemists of the country, and when the country's call went out for chemists the coöperation of this SOCIETY was a splendid substitute for any preparation the Government had to make. Almost instantly the Government was able to put its hand on the man who was needed for the particular job, to call him to Washington or service wherever he might be needed. Your SOCIETY was by its very existence anticipatory of the calling into being of the forces to collect these data, and the Government owes to this SOCIETY, therefore, a debt of gratitude for this closeness of association and intimate knowledge of the profession, which it was able to place at the Government's disposal and thereby to render the chemical knowledge of the country speedily available. The chemists did their share. They did it superbly.

The AMERICAN CHEMICAL SOCIETY sincerely trusts that it may never again be called upon to perform a similar service, but if it is so called its members will be found ready to serve their country in every field of duty.

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[1] *J. Ind. Eng. Chem.*, **11**, 921–24 (1919).

Milestones of Progress

The following are the chief milestones marking the steps of the SOCIETY'S progress:

Foundation, April 20, 1876.
Incorporation, November 9, 1877.
Journal of the American Chemical Society, January 1, 1879.
Reorganization on national basis, 1891.
First local section, January 21, 1891.
Chemical Abstracts, January 1, 1907.
Divisional organization, 1908.
Industrial and Engineering Chemistry, January 1, 1909.
Organization for national war service, 1917
News Service, 1917.
Monographs, 1920.
News Edition, 1923.
Regional meetings, 1923.
Journal of Chemical Education, 1924.
Chemical Reviews, 1924
Separate divisional meetings, 1925.

The Future

The AMERICAN CHEMICAL SOCIETY is justly proud of its growth and accomplishments during its fifty years of existence. They have been sketched all too briefly in the present review. The future of the SOCIETY is bright. The accomplishments of the past are small in comparison with the unlimited opportunities of the future. Chemistry, probably more than any other science, will point the way, and guide the steps, of our country's progress. The application of chemical research to the increase of the knowledge of mankind, to the development of our country's industries, and to the material prosperity and happiness of our people, is certain to bring results beyond the power of our present vision.

That increasing opportunities for service will come to the SOCIETY cannot be doubted. The problems and the duties of the future will be met as they arise. It has grave problems before it to meet the cost of recording the results of the activities which it itself catalyzes. The SOCIETY has within its membership all of the leading chemists of America. They constitute a body of scientists which is growing in numbers, in prestige, and in knowledge. There are no educational institutions in the world better equipped to turn out qualified chemists than those of America.

The chemists of America are united in the AMERICAN CHEMICAL SOCIETY. They will not fail, individually or collectively, to contribute their share to the future progress of our country and the world!

Harris & Ewing

CHARLES E. MUNROE
(1849–   )
President 1898

Alman & Co.

EDWARD W. MORLEY
(1838–1923)
President 1899

WILLIAM MCMURTRIE
(1851–1913)
President 1900

Harris & Ewing

FRANK W. CLARKE
(1847–   )
President 1901

C. E. Munroe was also a Charter Member; F. W. Clarke attended the Priestley Centennial in 1874.

PART II

REVIEWS OF PROGRESS IN VARIOUS BRANCHES OF CHEMISTRY IN AMERICA

1876–1926

CHAPTER VI

MINERAL CHEMISTRY

BY EDGAR F. SMITH

Introduction

In preparing this sketch on mineral chemistry, or mineralogical chemistry, if you please, as it has developed in the fifty years of the life of the AMERICAN CHEMICAL SOCIETY, the writer was at once impressed with the fact that many of the earliest independent investigations of American chemists were made in this particular field of chemistry.

For example, as early as 1798 Adam Seybert, a doctor of medicine, laid aside his profession and devoted himself to the study of minerals. His collection was quite unique. In 1814 it became the nucleus of the collections which have grown to splendid proportions in the halls of the Academy of Natural Sciences in Philadelphia. Indeed, for years, Seybert was the master mind in the domain of mineral chemistry in this country. It was this interest, no doubt, which led him to send his only son, Henry, to Paris for scientific training. After graduation from the École des Mines, on his return to his native city, Henry Seybert busied himself with minerals. It was he who first demonstrated the presence of glucinum in the mineral chrysoberyl.

Then, too, in recalling Silliman, the elder, one remembers that in the early years of 1800, which he spent in Philadelphia in the study of chemistry under James Woodhouse, he brought with him, in a candle box, the entire collection of minerals then owned by Yale University, hoping to find someone in the City of Brotherly Love whose knowledge of minerals might enable him to determine his specimens. Such an one he discovered in Adam Seybert, who could with authority tell what the specimens were.

Further, men such as Gerard Troost, William Keating, Lardner Vanuxem, and others were making worthwhile contributions to mineral chemistry in the first third of the nineteenth century and a little beyond.

American chemists should not, therefore, hastily turn aside from mineral chemistry, because it represents a chapter in which their progenitors were leaders and proficients. Again, minerals are definite, distinct chemical bodies. Hence, their constitution is worthy of study; their synthesis is most fascinating. In the field of organic chemistry, for example, the great variety, the beauty, the multiplicity, and, it might be added, the value of the more than 300,000 specimens claim, and have claimed for years, the best thought of chemists who have delighted in determining the constitution of these derivatives of carbon. But the enthusiasm resulting from the unraveling of the constitution of a mineral such as epidote, topaz, or vesuvianite has not been very contagious, the truth being that chemists have not succeeded in determining the constitution of many minerals—true chemical compounds—as has been done, for example, in the case of salicylic acid, indigo, and many other organic products. The problem is a difficult one. It calls for an almost superabundance of patience, for a thorough knowledge of a great list of elements, for the power of analytic generalization, etc. One may purify benzoic acid, oxalic acid, or sugar and be assured that the final product is free from all adventitious foreign material, but the purification of a well-crystallized specimen of garnet or pyroxene is almost heart-rending. Comparatively few chemists have had the courage and patience requisite to search for adequate methods of purification of the material offered by mineral chemistry. Some few methods, falling perhaps within the domain of physical chemistry, have been applied, but there it has ended.

Men of the type and spirit of Berzelius, Wöhler, Friedel, Des Cloizeaux, Wollaston, Marignac, and Haüy are needed. When they arrive, the chapter on mineral chemistry will be emblazoned with glory.

The cobalt bases, discovered by Frederick A. Genth, developed later largely through the efforts of Genth and Wolcott Gibbs, and certain French chemists, e. g., Fremy, seemed to be an enigmatical group, as regards constitution, until the talented, keen Werner of Zurich, reflecting upon methods of approach which had sprung up in the years succeeding the activities of Genth and Gibbs, so brilliantly laid bare that field of interesting derivatives. And was not the chapter on sugars in organic chemistry, often spoken of as a *terra incognita*, marvelously simplified and made to stand forth as one of the most brilliant chapters of organic chemistry by the indefatigable Emil Fischer?

Was it not also this gifted chemist who brought light into the albumins and other members of the field of animal chemistry, which had long resisted the efforts made to solve their constitution, yielding only when new and modern methods of attack were resorted to by him? These contributions are known to all chemists and gratitude has been expressed by thousands of human beings who were affected in one way or another by the epoch-making endeavors of Fischer. On one occasion, when approached by a young American chemist working in his laboratory, with the question as to what field of chemistry he should devote himself on his return home, whether to the organic field or some other, it was Fischer who promptly replied—"to the inorganic field; the great mineral wealth of your country offers magnificent opportunities for research bound to be of value both from the standpoint of pure science and that of industrial developments."

These preliminary remarks have been prompted by a love for mineral chemistry. All readers may not share it, and some may be disposed to look upon the suggestions as unworthy of consideration. So be it!

Activities of Five Past Presidents

The committee which has in charge the preparation of the present volume proposed that this chapter should deal with activities in the field of mineral chemistry on the part of five distinguished Past Presidents of the SOCIETY who, in the years of the SOCIETY'S existence, made worthwhile contributions in that particular domain. Naturally, in fifty years many American chemists have given themselves to the study of mineral bodies. However, it seems wiser that this story should revolve in a general way about these Past Presidents of the SOCIETY, four of whom have passed on, while the fifth continues with us, thinking and working with enthusiasm along the lines which for years he has so well and richly cultivated.

FREDERIC AUGUSTUS GENTH.—To present-day students of chemistry the name of Frederick Augustus Genth (1820–1893) may convey little. Briefly, he was born in 1820 in Germany, was carefully educated and came under the tutelage of such persons as Leopold Gmelin, Bischoff, Blum, Leonhard, Fresenius, Kopp, Liebig, and Bunsen whose chemical assistant he was for three years. In 1848 he came to America, making his home at first in Baltimore and later in Philadelphia. In the latter city, his real research work was done. Passing over the earlier portions, such as the ammonium cobalt bases, to save time and to bring him closer to the period in which our SOCIETY was founded, and of which he was a corporate member, it will suffice to review cursorily his contributions to mineral chemistry in the seventies, and in later years when he was President of the SOCIETY.

It is with some hesitancy that the writer speaks of this gifted man and chemist, because he may be unduly partial in judgment, as it was in his very early years as a chemist that he enjoyed the privilege of serving as assistant to Genth, and through various experiences came deeply to appreciate him and his comprehensive chemical knowledge. All this happened in the seventies when organic chemistry held sway in the minds of younger chemists about as physical chemistry does now, and as an enthusiast in the former the writer busied himself in his leisure moments with the making of substitution products in the great benzene series and in studying condensation products. Some of these were highly aromatic, and the odors emanating from his little laboratory were not to the joy of his chief, who patiently forebore from remark for awhile but eventually, in very firm words, gave his youthful assistant to understand that further activity with these aromatic benzene bodies must cease. This crushing mandate caused him to work at night when the laboratory was absolutely clear and he could be alone. Upon retiring from this night work, he took the precaution to lower and raise the windows so that by morning the atmosphere of the laboratory might be sweet and free from the "vile stuff."

However, the keen sense of smell of Genth enabled him (at least such was the inference) still to detect aromatic odors. Without comment the writer was invited to a little room until then locked to him. On entering he was surprised to see that everywhere were large glass jars filled with monazite sands. "There," said the Doctor, "is material for your future research." In short, it meant that for the next year or two great quantities of this material were to be studied under the supervision and direction of the Doctor, and together with the many new things in the way of elements, new at least to the writer, there emerged from that research an assistant who was a complete convert to inorganic chemistry. But that is another story. An abundance of zirconium in the form of sulfate was extracted and this particular product, at a certain point, was invariably appropriated by Genth, who would say, with a knowing look as he carried the material away, "Zirconium is not simple; there is another element concealed in it, and when I have leisure I shall endeavor to isolate it."

Very properly the reader may ask—but how about the research work of Genth himself in mineral chemistry? To begin, then, attention may be directed to his studies of the alterations of corundum. These began early in the seventies and continued for many years. Very few present-day chemists have read the results of that study. Those who have been so fortunate as to have done so will agree that an exceedingly interesting field in mineral chemistry was opened to all who care to consider the constitution of minerals. The first astounding thing is, how did these wonderful transformations of corundum take place? What forces were at work in the change, for example, of corundum to minerals like spinel, diaspore, bauxite, gibbsite, quartz, opal, smaragdite, zoisite, feldspar, tourmaline, fibrolite, cyanite, damourite, and a host of others not necessary to name? The investigation attracted comparatively few chemists. To them these pseudomorphs were enigmatical, and unless in the years which have since gone by earnest efforts have brought to light explanations for their occurrence, of which the writer is ignorant, they continue to be a chapter crying for further consideration and study.

In massive feldspar near Shimersville, Pennsylvania, was found, in 1882, a beautiful black, well-crystallized body. It seemed to be an isolated product but upon presenting it to Genth, he smilingly said, "It is an alteration product of corundum. It is tourmaline." Speculation as to its formation was rife, as were the transformations of corundum into other minerals without the loss of its crystallographic habitus.

On one occasion another distinguished chemist and Past President of our SOCIETY, as well as a close friend of Genth, journeyed from his distant home in the South to discuss with him an alteration of corundum into a substance resembling the mineral damourite. Genth had analyzed this alteration product and was quite certain that it was the mineral which it was supposed to be. Dr. J. Lawrence Smith presented analytical results pointing to the possibility of its being a new member of the family of micas. These eminent chemists were not disposed to enter into a public controversy; hence Smith spent several weeks in Genth's laboratory, the two men working side by side over the material in question. The problem was, perhaps, a minor matter but it beautifully illustrated the care and the accuracy with which Genth studied minerals. These two analysts differed a good deal from each other in the percentage of silica obtained as well as in that of alumina and other components of the supposed damourite. Numerous analyses were made by each. Genth's results were regularly concordant, while those of Smith varied greatly among themselves. Without entering into details, wearisome at best in this place, the discrepancies in Smith's results were found to be due to incomplete decompositions of the material as well as to indifference in the reduction of the mineral powder to a sufficient degree of fineness. Smith gladly accepted the outcome and the two friends continued to push forward other studies relating to the alteration of corundum. Chemistry students of the present period would probably shrink from the perusal of this classic memoir (Alterations of Corundum) in mineral chemistry, but its examination is bound to suggest lines of further investigation which, with all our modern facilities and methods of attack, and unusual exactness in analysis, ought to disclose results of profound theoretical value. One wonders how long it may be until the seeker after truth will turn his attention to some of the problems presented by this fundamental investigation.

It has been said that Genth was almost without a peer as a chemist, especially in analytical work, for he was familiar not only with the reactions and methods of determination and solution of the ordinary elemental and compound ions but, what is more remarkable, with the rarer and less frequently occurring ones as well. Further, all of his scientific work was characterized by a conscientiousness and fidelity to fact which was exceptional. No labor seemed to him too great if by it an added accuracy could be assured. Many personal laboratory experiences confirmed this view of the great exponent of mineral chemistry. Thus, a rare mineral, called "herderite," had been observed at Stoneham, Maine. It was a phosphate of glucinum and calcium. Specimens of the same mineral from a European locality were analyzed by Clemens Winkler, discoverer, a few years later, of the element germanium. In some unaccountable way this distinguished chemist had overlooked, in all his analyses, a fluorine content amounting to about nine per cent. To this omission attention was directed by Genth in several very concordant analyses, followed as might be surmised by an interesting and a bit acrimonious interchange of analytical experiences on the part of the two master chemists. Suffice to add, Genth emerged as the generally accepted victor.

Much attention also was given by Genth to the mineral vanadinite, particularly those specimens which came from New Mexico and which were first observed there by Silliman, the younger. This study brought as an associate to Genth the celebrated Gerhardt von Raht, to whom the crystallography of these interesting bodies fell as his special work. Several communications ensued. Again it was the hope of Genth that he might arrive at some definiteness in the constitution of the mineral, which constitution he finally announced as a combination of the chloroarsenate of lead with the chlorovanadate of lead. Had he followed the studies of his intimate friend, Wolcott Gibbs, upon the "complex inorganic acids," it is quite possible that he would have pronounced vanadinite to be the salt of a chlorovanado-arsenic acid. The correct interpretation of this particular mineral and allied minerals continues to await solution.

Genth rarely associated anyone with himself in his mineral studies, although in the latter years of his activity the very distinguished mineral chemist, Samuel F. Penfield, participated with him, rarely, however, doing more than such crystallographic research as was possible.

In addition to his more comprehensive papers, Genth was the author of twenty-three minor contributions in mineral chemistry which brought to the attention of the chemical public descriptions of new minerals. In fact, he was the discoverer of twenty-four new mineral species, all of which were so thoroughly individualized, both by chemical and by physical methods, that they took at once a position in the science which they have ever since maintained. To name them would be superfluous. Persons interested in perusing the original documents will be impressed with the astounding skill of the analyst, of which the writer had the most convincing proof, and which disclosed to him the fascinating power of the objects in mineral chemistry, the one regret being that the efforts to unravel constitution appeared so feeble that discouragement on the part of the student was apt to arise. And yet, in the light of the modern spirit of research, the fields opened up by Genth in mineral chemistry must be made intelligible to all who cultivate the science of chemistry.

J. LAWRENCE SMITH.—Reference in a preceding paragraph to Dr. J. Lawrence Smith (1818–1883), devoted member and Past President of our SOCIETY, brings into remembrance his work. In the now priceless photograph of American chemists who, on August 1, 1874, gathered about the last resting place of Joseph Priestley in Northumberland, Pennsylvania, there may be seen the friendly face of this chemist who had come from his distant Kentucky home that he might do homage to the memory of the discoverer of oxygen. There, too, he united with his confrères in the adoption of the motion of the young secretary of the gathering—Dr. J. Persifor Frazer—that an AMERICAN CHEMICAL SOCIETY be constituted. There the matter rested.

The name of Smith has many times been on the lips of chemists, brought there most frequently, perhaps, when the best method of decomposing silicates, with the object of getting at their alkali content, was the subject of comment. As the writer was favored with many opportunities of observing this celebrated chemist, whom he had often heard characterized as, "a man of great ability and great integrity of character; one who seemed to win all who came within the sunshine of his genial nature," there always comes to mind that Dr. Smith, at eight years of age, was studying algebra, and at thirteen years, calculus, so it was not surprising that before seventeen years of age he might have been discovered at the University of Virginia, busied with such subjects as chemistry, natural philosophy, and civil engineering, including advanced mathematics. His instructor in chemistry was John P. Emmet, under whose stimulus and that of others, including W. B. Rogers, his scientific studies were developed and further confirmed. Whatever attention he may have bestowed upon literary subjects must have been in his preparatory years in the old, aristocratic city of Charleston, South Carolina, where he was born in the year 1818, being, therefore, slightly older than his friend and co-worker, Frederick Genth. After two or three years Smith abandoned scientific pursuits for medicine, receiving his degree in 1840, upon the presentation of a thesis on "The Compound Nature of Nitrogen," soon thereafter journeying to Paris where he diligently attended instruction under Dumas, Orfila, Poulliet, Desprez, Becquerel, Dufrenoy, and Elie de Beaumont.

On one of his summer excursions he found himself at the door of Liebig's laboratory in Giessen, which accidental circumstance turned the whole course of his life to chemistry, from which it was never diverted. Both he and Genth had come under the inspiring influence of Justus Liebig. Hence, they had a somewhat similar training for the work in which they were to engage.

In his student days, Smith had devised a very delicate and most interesting test for the detection of barium, having also determined its quantitative value. This occurred in 1839, and probably there are many whose eyes will rest upon these lines who, like the writer, followed the method with his own students in analysis fifty years later.

As a result of his research upon the monazite sands of North Carolina, the writer was brought on one occasion into a lengthy interview with Smith, who had paid a visit to Genth, but finding him absent, in his friendly and sympathetic way, turned to the young assistant, inquiring as to his work, in which the distinguished scholar apparently took the very deepest interest. On the evening following this particular interview, Dr. Smith delivered a verbal communication before the Academy of Natural Sciences (Philadelphia) outlining in considerable detail his work upon samarskite, which he was conducting in Louisville. In his audience there chanced to be an assistant professor, an associate of the writer, who made it his particular business to inform Genth very early the next morning that Smith had evidently trespassed upon the study of his young assistant, the writer. Whereupon, without any further information, Genth reminded his assistant that he should not have made any communication upon this work, which was really his work, not even to Smith—his friend. There was just a bit of human nature, perhaps, in this, which in the end amounted to nothing, because the communication of Smith to the Academy related chiefly to the finding of columbic and tantalic acids in specimens of samarskite. Smith was, however, interested in the writer's work and so expressed himself a little later, because he had been occupied with cerium earths to which, at the time, he was giving a great deal of attention. These studies were discussed with his friend Genth, and it was quite natural that the writer should have heard much of their conversation, particularly the portion relating to the new element, mosandrum, about which Smith had addressed the Academy of Natural Sciences as early as 1877. The details of this remarkable study need not be given, suffice to mention that among his statements he informed Genth that a spectroscopic study of his material by Soret established without question the existence of a new earth and added:

> If we take their properties, their spectroscopic properties (meaning the cerium earths) we find didymia at one end of the group, mosandrum in the middle, and terbia at the other end giving absorption bands. In fact, it seems to need these two elements, terbia and mosandrum, to complete the groups.

The writer was filled with awe. He knew little in regard to absorption spectra but was deeply conscious that he was in the presence of one who had discovered a new element. So what harm could an unknown neophyte have done by fully telling the story of his own work! And thus Dr. Genth himself thought; so the writer continued in the good graces of his chief.

It may have escaped the memory of the majority of chemists that during the administration of President James Buchanan, the Turkish government applied to him for a scientist who might develop the agricultural interests of his Empire. Smith was selected for this purpose. During the years of his residence in Turkey he, however, became particularly absorbed in its mineral resources. Emery mines were discovered by him and in working these he came in contact with large deposits of massive corundum, as well as with the crystallized mineral. His report upon the same was highly regarded by men of science. The occurrence of the corundum claimed more than ordinary attention, and to intimate friends, living in the eastern part of this country, he addressed letters calling attention to the fact that possibly in their localities this mineral would be found, naming its associates as guides in their search for it. His prediction was correct. This observation is made to show that long before Genth and he became intimate, corundum, a pet or favorite study of Genth, was a study which occupied his friend's earnest endeavor. Hence, when in the seventies they were both engaged with an examination of alteration products of the mineral, it was quite natural that they should be occasionally brought into collision but, as has been shown, these differences were amicably adjusted when they worked side by side.

Probably the remarkable studies of Smith upon meteorites will be, for all time, regarded as his *magnum opus*. The collection of these strange bodies and the heroic efforts put forth to ascertain their minutest constituents challenge the admiration of every devotee of mineral chemistry. So ambitious was he in this research that his collection was regarded in its uniqueness and importance as one of the first in this country, if not in the whole world.

For a short period of his life Smith was professor of chemistry in the University of Virginia, in a certain sense his Alma Mater, and there it was that he, together with Professor Brush, afterwards the distinguished professor of mineralogy in Yale University, unceasingly pursued mineral analysis. In one of the earliest editions of Dana's "Mineralogy" their initials "B. & S." appear attached to the analyses of a vast group of minerals. So it is not surprising that the writer, in his personal conversations with Smith in Genth's laboratory, should have conceived for him a very human admiration.

The most important contributions to mineral chemistry made by Smith after the foundation of our SOCIETY were those that related to the minerals in which were present the so-called rare earths; that is, the cerium group of elements and the minerals containing columbic acid, tantalic acid, titanic acid, tungstic acid, and molybdic acid. In samarskite from North Carolina, for example, he was fortunate in bringing to light new minerals containing columbic and tantalic acids—these were hatchettolite and rogerite. He first called attention to the mineral tantalite, which had been observed in the state of North Carolina. His interest in the columbates and tantalates was great, and as an introductory to one of his very creditable mineral studies, he made a strong plea for the retention of the name "columbium" discovered in 1801 by Hatchett. He went into great detail of argument against the name "niobium."

Among his associates working along similar lines, he was constantly emphasizing the fact that one of the distinguishing characteristics of the mineral tantalite was its high specific gravity, never falling below 7, and he seems to have made it a habit when minerals of this group were brought to him as being tantalites to dismiss them at once as members of the columbite group if their specific gravity fell below 7. It is very doubtful whether Smith ever succeeded in evolving a complete separation of titanic acid from columbic and tantalic acids, although he made many earnest attempts in this direction. Neither was he any more successful in separating columbic and tantalic acids from each other.

To review all his work would be out of place here, yet the perusal of his experimental efforts in isolating the various components, of what was in those days termed "the cerium earths," made very plain his keenness, his untiring ,patience, and his ability as an analyst.

There is very little evidence, and that seems to have been of a passing character, that he made any attempt to explain the genesis of the minerals upon which he spent so much time and effort. Thus, he seems to have been quite content with Genth's views in regard to the origin of corundum. To the close of his life he was devoted to mineral chemistry; but, "he set aside the views of Chevreul that spermaceti was a fat, and reached the conclusion that it was a compound *ethal*, and that by its distillation a molecule of ethalic hydrate and *cetine* was produced. He further demonstrated by the action of potash on cholesterine, that the latter was nearly related to spermaceti." This was a peep into organic chemistry! He loved all chemistry and had joy in its pursuit. His studies command the respect of the entire scientific world.

T. STERRY HUNT.—Among the Past Presidents of the SOCIETY, justly regarded as a chemical philosopher, was T. Sterry Hunt (1826–1892). His scientific interests, strongly developed under Silliman, the elder, extended over a wide range, but in them all he worked from the standpoint of a chemist.

He has been properly credited with having originated the theory of simple water types, and in his earlier papers the germs of the ideas usually attributed to Gerhardt may be found. His researches upon the equivalent volumes of liquids and solids were a very remarkable anticipation of Dumas. In his introduction to "Organic Chemistry" (1852) he first defined that branch of chemistry as the chemistry of carbon and its compounds. To follow him into the field of pure chemistry would require years of steady application. From the fact that he gave himself, at the beginning of his professional life, to geological work, one is not surprised to discover him occupied with experimental work in mineralogy, emphasizing the importance of better analytical work in the field of mineral chemistry, and also the pressing needs of a better understanding and comprehension of the constitution of minerals.

His book entitled, "The New Basis of Chemistry," published in several editions, is a striking work and elicited much discussion. That it was thought to possess value is shown by its appearance in a French and also in a Russian translation. One of his last pieces of literary endeavor was a "Systematic Mineralogy" according to a natural system (1891). Its chapters are thought-arresting. They give evidence of broad training, and show very conclusively how the experiences of his years of experimental work brought to him many original and surprising views. It is impossible to give even an outline of all that he did in mineral chemistry; hence the reader must be content with a concise statement which will indicate his interest in the constitution of minerals—real chemical compounds.

It was Hunt who proposed to regard charcoal, graphite, and diamond as so many "polymeric modifications of elemental carbon." This idea of polymerism clung tenaciously to him, and although the law of progressive and homologous series had at that period been recognized in the hydrocarbon series, only Hunt felt that it might be extended to other compounds, believing it would lead, as it happens to do, to the conclusion that the chemical formulas of many mineral species are very complex and have molecular weights very much higher than those admitted for hydrocarbons and their derivatives. There is no doubt but that this assignment of complex formulas of high molecular weights and of homologous relations to minerals originated with Hunt. To minerals such as pyroxene, amphibole, wollastonite, albite, anorthite and orthoclase, he ascribed very complex formulas.

It will be remembered that the doctrine of progressive series had been enunciated first by James Schiel of St. Louis, Missouri, and later by Charles Gerhardt. Hunt attempted to extend this doctrine to other compounds, maintaining that bodies differing by $(OH_2)_n$, $(OM_2)_n$, and $(SM_2)_n$ might, like those differing by

$(CH_2)_n$, be homologous, and so he applied the principles of the progressive series of organic bodies to members of the mineral kingdom. While he regarded himself as the first to make such an application, he was yet aware that the doctrine of progressive series in inorganic bodies had been attempted by other chemists. For example, his intimate friend, Wolcott Gibbs, described the polytungstates, in 1877, as a homologous or progressive series. The words of Hunt himself declare that:

> The extension of the doctrine of homologous series to minerals serves further to show the importance of small variations in the composition of definite crystalline members since very small portions of different substances may not only occur as necessary elements in such a compound, but may even change essentially its chemical relations * * * In such compounds partial substitutions and small additions affecting but slightly the centesimal composition of a species may nevertheless be as essential to its chemical composition as the small amounts of silicic and phosphoric acids added to polytungstates. Such substitutions and additions would, however, if found in ordinary analysis of mineral species be disregarded as impurities not essential to the composition.* * * Further and more critical chemical analyses are necessary before we can fully know the constitution of dense, insoluble species, and the great difficulty is to decide how far these small portions of elements are due to impurities and how far they are elements necessary to the constitution of the species, questions which in many cases can only be solved by much care and study. It is well to remember in this connection the effect of minute quantities of various elements in modifying the characters of metals.

The researches of Wolcott Gibbs upon the derivatives of complex inorganic acids, as well as the studies of others who busied themselves with this group of chemical compounds, greatly influenced the thought of Hunt. It had been observed time and time again that 0.10 per cent of some constituents affected the crystalline character and the physical and chemical properties of the products in an astonishing way. Other observations of Wolcott Gibbs also determined the thought of Hunt in regard to the constitution of minerals, particularly that of the silicates. Gibbs called attention to polytungstates in which pentoxides formed very definite compounds with the tungstic acid, and demonstrated that the lower oxides and the pentoxides, such as the trioxide and dioxide, might all combine with the tungstic acid to yield a complex anion which, in turn, united with some one of the many protoxides to form definite derivatives. So in the course of his deliberations Hunt began to query as to whether the alumina in silicates, such as orthoclase, did not function as a part of an acid radical which, with the protoxide of potassium, yielded the mineral. Very definite products had resulted from the union of aluminum oxide with tungstic acid and also with molybdic acid.

Perhaps some readers will recall that among students of mineral chemistry there used to arise the question as to the function of boric acid in tourmalines. It was imagined that this acid or its oxide had replaced a portion of the aluminum oxide. That was not a very satisfying explanation but in the light of the production of borotungstates, in perfect harmony with the aluminotungstates, the conclusion was that the complex anions in the polytungstates and polymolybdates were quietly existent also in complex silicates. The writer ventures to add that when the constitution of the derivatives of the complex inorganic acids has been made clear the constitution of many complex bodies in mineral chemistry will be rapidly unraveled.

Hunt said, after reflecting upon the results of the brilliant studies on sugars by Emil Fischer, that they were of great significance, and that although such methods of investigation as disclosed the nature of the sugars could not be applied to fixed and insoluble silicates, there was no certainty that in the case of mineral oxides, sulfides, and silicates we are not dealing with bodies which, while physically very similar, have differences in constitution as great as the sugars. When we pass from bodies like the sugars, made up of but three elements united in simple ratios to others far more complex, like the cobaltamines, the polymolybdates, and the polytungstates, we learn that the simplest admissible formulas of these lead to molecular weights of thousands, as in the borotungstate of Klein and in the hydrophosphovanadotungstate of barium first described by Gibbs.

The chemist who, with such facts before him, attempts to calculate, from the results of chemical analysis, formulas for the chlorites, the micas, the epidotes, and the tourmalines, soon finds how inadequate are the principles ordinarily recognized and is led to conclude that did we possess a knowledge as complete for these natural silicates as for the artificial bodies we should find that our present formulas for these silicates are but approximations.

This imperfection must pertain to all our formulas for mineral species except such as calcite, barite, fluorite, and for some metalline sulfides and arsenides, which for purity and definiteness may be compared with artificially crystallized substances.

Such are some of the generalizations of Hunt as late as the nineties. They indicate that although he was the discoverer of new minerals and a devoted student of geology, a predominating idea with him was the constitution of minerals as definite chemical compounds. He naturally recognized the inefficiency of all then known methods for that purpose. His observations on the elucidation of this problem are set forth in no uncertain language in his "Systematic Mineralogy." His theoretical views were welcomed. They were supplemental and should have earnest consideration. They are very suggestive. They have been overlooked to a large degree by many students of mineral chemistry. Various reasons are contributory to this omission.

Although born in the United States, Hunt spent many years in teaching science in Canada, where he became a leader in geological and mineralogical circles. The impression made there was a very deep one. He returned to the United States in 1872, accepting the chair of geology in the Massachusetts Institute of Technology made vacant by the resignation of William B. Rogers. Hunt was also present at the memorable gathering of American chemists about the grave of Priestley in Northumberland, Pennsylvania, on August 1, 1874, where he delivered an inspiring address.

This tribute was paid Hunt upon retirement from academic life:

> Long an indefatigible experimenter and an extensive observer, Hunt was also an original and philosophical thinker and took an influential part in the establishment of the most matured and scientific theories. He was early in the field of chemical speculation and aided essentially in the revolution of views which has ended in the establishment of a new chemistry.

Refreshing, indeed, is it to know that so brilliant a mind had devoted years to the problems of mineral chemistry.

WILLIAM FRANCIS HILLEBRAND.—It was late in 1878 or early in 1879 when the administration of the newly organized United States Geological Survey advised an inquirer, "that it has just been decided that there would be no opening for a mineral chemist." The modest inquirer was William Francis Hillebrand (1853–1925). In 1880 S. F. Emmons, in charge of the Rocky Mountain Division of the Survey, "asked me (Hillebrand) if I would like to take a position as chemist in his Division of the Survey. Thus was offered me from a clear sky the very position I had sought when applying to Mr. King. Of course the offer was accepted." And so began the career of one of the most distinguished and able Past Presidents of our SOCIETY.

At the close of his preparatory studies in the United States he might have been discovered in 1872 as a matriculant of "Old Heidelberg," pursuing studies under Bunsen, Kirchhoff, Blum, Leonhard, the younger, and Karl Klein.

He has left us so recently that nearly every member of the SOCIETY will recall his face and figure. His modesty and silence generally placed him more particularly among his intimates so that his addresses were not frequently before the public.

His accomplishments in the vast field of mineral chemistry are, however, fresh in memory. Yet it will be worth while to let pass in review such of his achievements as stamped him a great force in the field of mineral chemistry. Although relinquishing every claim to being an organic chemist, his close friends know that while in the University of Strassburg with Fittig he unfolded the constitution of quinic acid. Genth, J. Lawrence Smith, and Hunt, his predecessors in this group of mineral chemists, also did noteworthy work in the organic domain.

The old Freiberg Mining Academy appealed to Dr. Hillebrand, for there was supplemented "his experience in mineral analysis gained with Bunsen." To return, however, to his contributions to mineral chemistry, analysts universally will declare his "Analysis of Silicate and Carbonate Rocks" a work of paramount importance. The favorable reception given it amply attests this. It was the product of a master mind—of a chemist to whom analysis made a powerful appeal. Many, of course, are indifferent to it. It exasperates them. They would cast it aside. In the words of Wolcott Gibbs, they look upon it "with contempt." But it means everything to those striving to get a better knowledge of the constitution and deportment of minerals which, as we admiringly gaze upon them in their most attractive forms, seem to smile and defy us to pull them apart and reunite their components as has been done for numerous organic derivatives.

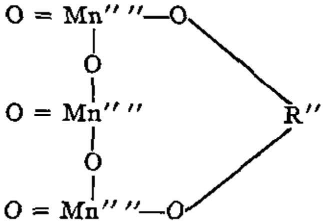
Like Genth, Hillebrand was most solicitous as to purity of mineral material, of reagents, of the accuracy of methods pursued, and also as to the determination of the minute quantities of the components which perchance were present, a fact also constantly emphasized by Hunt.

The marvelous patience, the keen discernment, the intelligence manifest in his "System" command the respect and gratitude of every student who wishes for a clearer vision in the domain of mineral chemistry.

His discovery of nitrogen in uraninite was indeed epoch-making! He constantly said that that "gas was well worthy of further examination," and to Sir William Ramsay wrote: "It doubtless has appeared incomprehensible to you in view of the bright argon and other lines noticed by you in the gas from cleveite, that they should have escaped my observation. *They did not.*" Urgent duties of his official position prevented his aggressive pursuit of this point. The modesty and nobility of Hillebrand shine forth in his beautiful letters to Ramsay.

His studies of minerals evince the interest he had in them. What really is their constitution, he must often have asked himself. Corroboration of this query is plain in his discussion of the nature of a new mineral which he designated "coronadite."

> If this mineral is to be regarded as anhydrous the comparatively simple formula $R''(Mn_3O_7)''$ is quite satisfactory and may be written structurally:



> * * * Such intricate formulas as this should not cause the least surprise, however unlikely they may at first appear to be. The great number of manganites in varying degrees of saturation observed in nature and prepared artificially, some of them of even greater complexity than the above, are certainly not all mixtures of only a few simply constituted molecules. * * * From the known tendency of these bodies to form under laboratory conditions which may very well be repeated in their general character in nature, it is to be expected that a vast number of mineral manganites should exist, and it ought rather to excite surprise than otherwise if two or more are not formed simultaneously from the same solution. This, together with inherent difficulties of analysis, would offer a simple explanation of the fact that so few of the analyses may lead to rational formulas, etc.

His conclusions upon carnotite were also quite convincing—viz., that it was probably a mixture of minerals, the exact nature of which analysis fails to reveal, and he added:

> Instead of being the pure uranyl potassium vanadate, it is to a large extent made up of calcium and barium compounds. Intimately mixed with and entirely obscured by it is an amorphous substance—a silicate or mixture of silicates—containing vanadium in the trivalent state probably replacing aluminum.

A great deal more might be written upon his endeavor to gain a fuller insight into minerals.

On assuming the duties of chief chemist in the Bureau of Standards (1908), "his new duties lessened his activity in his favorite field, but did not entirely prevent him from sending out further communications relating to the composition of minerals."

Many will recall his more intimate talks upon the wonderfulness of the constitution of minerals!

FRANK WIGGLESWORTH CLARKE.—Reference to the reports of the United States Geological Survey, to the pages of the *American Journal of Science*, and the various chemical journals in this country, will disclose a vast amount of material submitted by Frank Wigglesworth Clarke (1847–), a former President of the SOCIETY who, throughout his entire career in chemistry, has been an ardent advocate of the study of mineral chemistry. In his numerous addresses and in popular, as well as in scientific communications, he has steadily held high this most worthy chapter of chemistry. His personal studies confirm these statements and one is really overwhelmed on a careful perusal of what he has effected in the way of elucidating the constitution of various mineral groups.

The value of his material is too extensive for condensation and is also too suggestive and, in many instances, too conclusive to be reviewed except in the most elaborate way; but no further excuse need be made for the conciseness of the statements of the labors of Dr. Clarke in this place.

Clarke emphasized the importance of analysis in mineral chemistry, being as jealous, indeed, of all improvements in this direction as any of his predecessors, but he has published much upon the constitution of mineral bodies. In his own words:

> A constitutional formula must fulfil several conditions. It must adequately express the composition of the mineral, covering all its variations; it must be readily applicable to the full discussion of analyses so that the different isomorphous salts which are commingled in a mineral species can be separately identified and given reasonable expressions; finally, it should indicate the relations between a species and the other minerals with which it is allied or into which it commonly alters.

Before the writer lies a beautiful specimen of black tourmaline. According to Clarke the micas seem to be most nearly akin to it, as he declares, "in each group we have to consider comminglings of isomorphous molecules and when tourmaline alters a mica is commonly the product of the reaction." The black tourmaline to which the writer has referred is the common iron tourmaline and from it have come muscovite and biotite.

If space permitted it would be interesting to follow Clarke in his further discussions of tourmaline, which has not yet been synthesized. He says all chemists who of later years have discussed the composition of tourmaline agree in giving the ratio 2:1 between silicon and boron, and offers a number of formulas which he regards as expressing the composition of the tourmalines. In them he assumes that tourmaline is a mixed salt, containing distinct boric and silicic radicals, while he is willing to admit that

> future investigations may prove that it is really derived from a complex borosilicic acid as yet unknown, and the same conception may be true of other minerals, such as axinite, datolite, etc.* * * A series of borosilicic acids is theoretically conceivable and until that question has been considered, the constitution of all the minerals mentioned under tourmaline must be regarded as unsettled.

May not the suggestions of Sterry Hunt, Wolcott Gibbs, and others who have occupied themselves with the derivatives of complex inorganic acids be fraught with a great deal of import; which is to say, that if these bodies which have been built up could be carefully worked out as to constitution, the methods adopted with them would enable the student of mineral chemistry to make decided advances in the deduction of the constitutional formulas of native complex products in the mineral world.

Considerable thought was given by Clarke to another extremely interesting mineral called "roscoelite," which he demonstrated as being essentially a vanadium muscovite. He modestly says:

> This constitution seems to be fairly well established. If that view be correct then two-thirds of the aluminum content have been replaced by vanadium and that this replacement is altogether likely is demonstrated by the fact that true vanadium alums have been prepared.

Analcite is another mineral which has undoubtedly attracted thousands of persons interested in mineralogy. Many chemists have queried as to what its true constitution was, as so many different formulas, written in various ways, were said to represent it. It contains one molecule of water which seemed to be a disturbing factor, but in Clarke's hands this difficulty was surmounted and he concluded that its minimum molecular weight was represented by four times its empiric formula. The water in the mineral exists there as water only, not as hydroxyl, for the reason that it was extracted by heat without destroying the crystalline nucleus, the anhydrous salt, hence he adds:

> If analcite, instead of being a metasilicate, is really a mixture of ortho- and trisilicate, then all of the analyses are intelligible. In nature analcite may be derived either from albite or from nephelite.* * * Its closest analogue, leucite, has yielded pseudomorphs of orthoclase and laeolite, while leucite and analcite are mutually convertible each into the other.

These examples indicate the problems pressing in from all sides in mineral chemistry. If the student of chemistry be desirous of engaging in the unraveling of profound chemical problems, he will find them in almost inexhaustible stores in that field. The keenness and far-sightedness exhibited by Clarke in the elucidation of this chapter command world-wide respect. Undoubtedly it was his devotion to this problem that led some years after to the preparation of "Data of Geochemistry," now in its fifth edition, a work that certainly is deserving of the study of chemists. It possesses astonishing merit. Whoever reads the chapter on metallic ores will turn from such a perusal with new thoughts on mineral chemistry. The number of syntheses which have been made in various parts of the world impresses one very deeply and cannot fail to inspire enthusiasm for the field of synthetic mineral chemistry. Would that more work of this nature might be done here in America!

Conclusion

But this story must stop. In the very brief and incomplete presentation of the vast achievements of five of the Past Presidents of the SOCIETY in mineral chemistry, during the lifetime of the SOCIETY, there is given a glimpse of the unsolved problems.

These five Past Presidents, Genth, Smith, Hunt, Hillebrand, and Clarke, were all teachers who inspired hosts of younger chemists; and, were the successes of the pupils of these masters combined with those of the latter, it might be truly said, so far as mineral chemistry is concerned, that they

"have placed our Nation's fame among the stars."

CHAPTER VII

PHYSICAL CHEMISTRY

BY WILDER D. BANCROFT[1]

Early History

The period of physical chemistry in America really began with J. P. Cooke, who lectured at Harvard on the New Chemistry over fifty years ago. He seems to have been the first man to include the concept of the absolute temperature in lectures to chemists. Cooke called his subject "chemical physics" and he labored alone so long that, when the physical chemistry of Ostwald, van't Hoff, and Arrhenius appeared, he did not recognize it as the normal development of his viewpoint. That was a pity; but it is a fate that comes often to pioneers.

The famous monograph on equilibrium in heterogeneous systems by J. Willard Gibbs is in some respects one of the most remarkable scientific articles that has ever been written. Gibbs was possessed of marvelous and apparently unerring insight; but the gift of expression was denied to him. It is not too much to say that Gibbs wrote in hieroglyphics and that a great part of his manuscript is still undeciphered. We know now that we can find in it the chemical potential, the phase rule, and the theory of osmotic pressure; the theory of electromotive forces, the Donnan equilibrium, and the theory of emulsification. We feel certain that some day we shall find in it theories in regard to all sorts of other things; but we do not know when we shall find them. It used to be popular to ascribe the negligible influence which Gibbs had then had on the development of physical chemistry to the fact that his monograph was published in the *Transactions of the Connecticut Academy;* but that fiction cannot be maintained. Everybody knows about Gibbs now; but the only way that one

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[1] There will usually be differences of opinion as to the relative or absolute value of almost any piece of scientific work, and the physical chemists of America are, fortunately for us, extremely individualistic. The opinions expressed in this article are my own and are not necessarily those of the AMERICAN CHEMICAL SOCIETY or of any of its other members.

can find anything new in Gibbs is to discover it independently oneself and then to look it up in Gibbs.

Carey Lea was another pioneer who had no immediate followers. His work on colloidal silver and on the photohalides was remarkable for those days; but the time was not ripe for it. The same thing is true of the work of Barus on the two-phase nature of colloidal solutions. R. B. Warder published work on the rate of saponification of the esters by alkali before Reicher did; but he was not a van't Hoff and he did not have van't Hoff behind him as Reicher did, so the real development was done in Holland and not in America.

The continuous development of physical chemistry in America began in the late eighties when the American students started studying with Ostwald. Morris Loeb was the first to come back; A. A. Noyes was a little later; and the first chair in physical chemistry was founded at Cornell in 1895. The early work consisted in the development of the ideas of van't Hoff, Arrhenius, and Nernst, as expounded by Ostwald; and of the phase rule theory of Gibbs, as expounded by Roozeboom.

Electrolytic Dissociation Theory

While the American physical chemists have, with a few exceptions, been enthusiastic adherents of the electrolytic dissociation theory, the exact measurements and the theoretical developments by A. A. Noyes and his collaborators have changed it to such an extent that there is practically nothing left of Arrhenius' original theory except the conception of ions as independently existing substances. The study of solubilities soon presented such difficulties that Noyes advocated what he called "the dismemberment of the mass law." He threw over the calculation of the dissociation from the molecular conductance and clung to the constancy of the solubility product. Arrhenius showed that the concentration of the undissociated salt is not always constant, which played havoc with the positive part of Noyes' program; but the calculation of electrolytic dissociation presupposes that the migration velocities of the ions are independent of the concentrations, a state of things which we know not to be true in many cases and which may not be true in any case. The carefully made experiments of Noyes, Coolidge, and others on the conductance of salt solutions at different temperatures showed conclusively that the Ostwald dilution law described the facts only for moderate dilutions and then only for weak acids and weak bases. A number of empirical modifications of the dilution law have been suggested—many of them by Americans; but not one is really satisfactory. Making use of the van der Waals formula or of the Keyes equation of state merely adds to the complexity.

Different people have tried different ways of getting at a more exact theory. Morse showed that mass concentrations were better than volume concentrations for calculating osmotic pressures, unfortunately without referring to what van't Hoff had said previously on this point, and thereby missing that the important thing is the volume occupied by the solvent in the solution and not the volume of a given mass of the pure solvent. Jones developed a hydrate theory on the explicit assumption that the van't Hoff-Raoult formula holds absolutely when one chooses the constituents properly. At Cornell we emphasized the statement by van't Hoff that the formula cannot hold if the heat of dilution is not zero. Hildebrand, at the University of California, discards the van't Hoff part of the formula completely. The question of compounds in solution has been considered by Kendall, at Columbia, with reference to freezing points, and by Bingham, at Lafayette, with reference to fluidity. Morgan, at Columbia, has followed the lead of Ramsay and Shields, specializing in associated liquids. The Ostwald theory of indicators has been shown to be inadequate in detail, though sound in principle, and Stieglitz has been influential in developing the chromophoric theory.

Kahlenberg in America, H. E. Armstrong in England, and Traube in Germany are the three irreconcilables, who do not believe at all in the electrolytic dissociation theory. While they have not accomplished what they set out to do and are not likely to, it is interesting to note what Walden has said on this point.

> Both Traube and Kahlenberg have helped along the electrolytic dissociation theory by their criticism of it The deliberate emphasis on the overhasty generalizations (for instance that all reactions are ion reactions), the logical criticism of the insufficiently explained causes for the dissociation into ions, and the contradictions in the enormous fields of non-aqueous solutions which often rested on inaccurate observations, the planning and carrying out of his own clever experiments on instantaneous reactions in non-conducting solutions, all these can be considered as positive achievements by Kahlenberg because they made it necessary for the upholders of the dissociation theory to make new experiments to clear up their own views, to make limitations, to reconsider their assumptions.* * * Quite irrespective of whether Kahlenberg succeeds in accumulating enough dynamite to destroy the osmotic and electrolytic solution theories, his experimental work is full of interest, because it calls attention to a neglected field, which one can consider as a borderland between organic chemistry and physical chemistry.

The work of Franklin, Cady, and Kraus on solutions in non-aqueous solvents shows that there are many cases where the electrolytic dissociation theory has much harder sledding than in aqueous solutions.

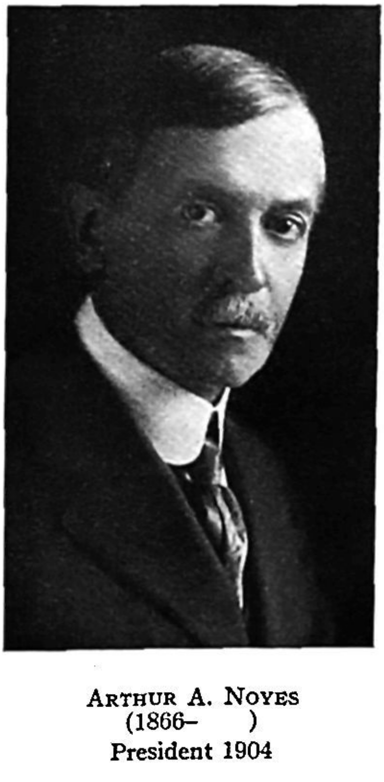
Sutherland was the first to suggest that electrolytes are really dissociated completely at all concentrations, and this view has been adopted by A. A. Noyes, Debye, Brönsted, Bjerrum, and others since the X-ray study of sodium chloride crystals has made it plausible that there are no molecules in these crystals. Harkins recognizes at least three types of dissociation, for he says that a tenth-normal solution of sodium chloride is 100 per cent polarized or ionized, 85 per cent electrolytically dissociated, and 68 per cent thermodynamically dissociated. This is an epigrammatic way of saying something else. If sodium chloride crystals are 100 per cent polarized or ionized, Harkins asserts that they must be the same in solution, though this seems to prove too much because the reasoning would seem to apply equally well to non-aqueous solutions. With regard to the other two dissociations, Harkins merely means that the apparent dissociation, as calculated from the conductance, is 85 per cent, while it is 68 per cent when calculated from solubility determinations, electromotive force measurements, etc.

Lewis has gone one step farther and considers ionic concentration as a rather meaningless phrase.

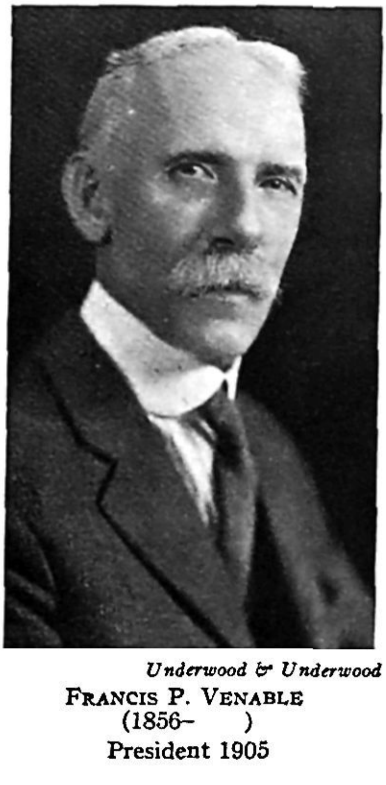
> It may be of interest to view for a moment the logical implications of such a term as "degree of dissociation." Let us consider the equilibrium in the vapor phase between diatomic and monatomic iodine, and at such a temperature that, on the average, each molecule of I_2, after it has been formed by combination of two atoms, remains in the diatomic condition one minute before it redissociates. During this minute such a molecule will traverse several miles in a zigzag path; and, after its dissociation, each of its constituents will traverse a similar path before it combines once more with another atom. If we imagine an instantaneous photograph of such a gaseous mixture, with such an enormous magnifying power as to show us the molecules as they actually exist at any instant, then by counting the single and double molecules we should doubtless find the same degree of dissociation which is actually determined by physicochemical methods.
>
> On the other hand, if we should choose a condition in which the dissociation and reassociation occur 10^{13} or 10^{14} times as frequently, the atoms of the dissociated molecules would hardly emerge from one another's sphere of influence before they would combine once more with each other or with new atoms. In such a case the time required in the process of dissociation would be comparable with the total time during which the atoms would remain free, and even our imaginary instantaneous photograph would not suffice to tell us the degree of dissociation. For, first, it would be necessary to know how far apart the constituent atoms of a molecule must be to warrant our calling the molecule dissociated. But such a decision would be arbitrary; and according to our choice of this limiting distance, we should find one or another degree of dissociation.
>
> Until a problem has been defined logically, it cannot be solved experimentally; and it seems evident in such a case as we are now considering that, just as we should obtain different degrees of dissociation by different choices of the limiting distance, so we should expect to find different degrees of dissociation when we come to interpret different experimental methods. Now it is generally agreed that ionic reactions are among the most rapid of chemical processes, and it is in just such reactions that we should expect to find difficulty in determining, either logically or experimentally, a really significant value of the degree of dissociation.

Ira Remsen
(1846–)
President 1902

John H. Long
(1856–1918)
President 1903



Arthur A. Noyes
(1866–)
President 1904



Underwood & Underwood

Francis P. Venable
(1856–)
President 1905

> On the whole, we must conclude that the degree of dissociation and the concentration of the ions are quantities which we cannot determine by existing methods, and which perhaps cannot be defined without some degree of arbitrariness. The question is one which should be left open, especially as its answer is of no immediate concern to those who employ purely thermodynamic methods.

Gibbs has gone to the other extreme and has deduced Henry's law for the case where there is only one molecule of the solute, even though it cannot, by definition, be in both phases simultaneously.

A phenomenon which appears to bear out Lewis' contention is the so-called neutral salt effect. If we take a tenth-normal hydrochloric acid solution and add enough sodium chloride or bromide, it is a simple matter to bring the apparent concentration of hydrogen ion up to half-normal or more, which is absurd whether we consider tenth-normal hydrochloric acid as 100, 85, or 68 per cent dissociated. Lewis has got round this difficulty, as well as others, by introducing the conceptions of fugacity, activity, activity coefficients, etc., working with activities instead of concentrations. Speaking roughly, the activities are the values which the formulas under consideration do give, and consequently they satisfy the formulas with any desired degree of accuracy.

For a while the concepts of fugacity and activity did not appeal to the chemists; but the lack of any more satisfactory explanation has led people to take up this viewpoint. Debye in Switzerland and Brönsted and Bjerrum in Copenhagen are strong for it. In America a number of the younger chemists are spending most of their time measuring activity coefficients.

It must be admitted that the electrolytic dissociation theory has suffered much more from its friends than from its foes. Forty years of intensive development have brought us to the point where we cannot determine any electrolytic dissociation with any degree of accuracy and where we question the significance of the term "electrolytic dissociation." The range over which our formulas apply has decreased and it is not much of an exaggeration to say that the really orthodox physical chemist now looks upon a hundredth-normal solution as a moderately concentrated one. A situation like this cannot last, because physical chemistry must deal with actual solutions and not limit itself to a study of slightly polluted water. Water analysis deals with parts per million; but physical chemistry should not be restricted to this. It is probable that the Semicentennial of the AMERICAN CHEMICAL SOCIETY will mark the beginning of a new period.

It is easy enough to point to one factor which has been neglected practically completely and which may be the one which has caused most—and perhaps all—of our difficulties. For years H. E. Armstrong in England has chided the physical chemists for considering water only as water, whereas it is a complex and variable mixture. This criticism seems well founded; but, unfortunately, Armstrong has never succeeded in showing what could be done with his idea and consequently the idea has been valueless hitherto. Everybody admits that water is a polymerized liquid and that the degree of polymerization may change on the addition of electrolytes. This is the orthodox way of accounting for the displacement by salts of the temperature at which the maximum density of water occurs. Sutherland, Lewis, McBain, and others have suggested such a displacement of equilibrium as a possible source of error in our physical chemistry calculations; but nobody seems to have made a serious attempt to see how adequate this suggestion really is.

In the case of the dilution law, a change in the degree of polymerization of water with the concentration means a change in the solvent or in what Washburn calls "the thermodynamic environment." This carries with it a change in the dissociation constant. We do not know to what extent this hypothetical displacement of equilibrium will account for the discrepancies between theory and experiment; but it is a factor which has not been taken into account quantitatively. In the electrometric determination of hydrogen-ion concentration, we are really measuring the difference of chemical potential and we calculate the data into concentrations on the explicit assumption that there has been no change in what Nernst calls "the solution pressure" and which is really the difference in the free energy levels for unit concentration. Increasing the chemical potential of the hydrogen ion is equivalent to decreasing the solution pressure of hydrogen. It is possible theoretically to increase the chemical potential of the hydrogen ion without necessarily increasing its concentration. Lash Miller has shown that adding alcohol to a sugar solution increases the chemical potential of the sugar because it decreases the solubility of the sugar. Consequently, the measured pH of a solution does not necessarily show anything about the actual concentration of the hydrogen ion. We usually say that the color change of an indicator, phenolphthalein fot instance, occurs at a definite hydrogen-ion concentration. This is a careless, and sometimes an inaccurate, way of speaking. What we really mean is that the color change occurs at a definite chemical potential of the hydrogen ion, when there is no salt error.

For this case Lewis' activity is another form of Gibbs' chemical potential, and the Gibbsian way of putting it is better because we know that there is another term in the chemical potential beside the concentration term, and consequently we realize that the two must be studied separately. In other words, there are two independent variables jumbled together and hidden in the activity concept but kept clearly distinct when we speak in terms of the chemical potential.

There is no reason for despondency about the electrolytic dissociation theory and about concentrated solutions until after we have determined the effect of the changing polymerization of water on our formulas; and by that time there may be no cause for despondency. It is worth noting that McBain suggested, seven years ago, that the effect of a neutral salt upon the volatility of acetic acid was due to a change in the chemical potential; but it is clear that he did not realize the tremendous significance of that remark.

In two cases which have been studied recently, the importance of the liquid equilibrium stands out clearly. It seems practically certain that the peptization of gelatin by potassium iodide solution is due to the displacement of the water equilibrium by the potassium iodide. Since the action of the potassium iodide can be duplicated by raising the temperature, the peptization is due to depolymerized water. The reverse case is to be found in the ether-alcohol peptization of pyroxylin, where the ether changes the degree of polymerization of the alcohol. Since alcohol does not peptize pyroxylin when heated and does when cooled way down, it must be the polymerized alcohol which peptizes the pyroxylin. A sol which is quite fluid at low temperatures becomes a soft, flowing jelly at room temperature, and a stiff jelly at 120° C.

An important contribution to the study of reaction velocity was made by A. A. Noyes. Wilhelmy had determined the order of reaction by seeing whether a good constant is obtained over the whole run or nearly so, and this is the method which is used ordinarily. Harcourt and Esson adopted the plan of making all concentrations but one relatively large so that only one component changed appreciably in concentration and they then determined the order of the reaction for that component. This was afterwards formulated a little more definitely by Ostwald and is often credited to him. For gas reactions van't Hoff determined the order of the reaction direct from the differential coefficients; but nobody realized the value of this method until it was resurrected by Noyes, who showed that the time necessary for a reaction to run half-way is proportional to log 2 for a monomolecular reaction (i. e., independent of the initial concentration); $1/A$ for a bimolecular reaction (i. e., inversely proportional to the initial concentration); and $3/2A^2$ for a trimolecular reaction (i. e., inversely proportional to the square of the initial concentration). By varying the initial concentration sufficiently, differences were obtained which quite overbalanced the secondary disturbances that are liable to vitiate the conclusions based on the other two methods. This method, that Noyes adapted from van't Hoff, changed our views completely in regard to many reactions which had been studied prior to that time. At the Toronto laboratory under Lash Miller work was done for several years on reaction velocities in systems containing oxidizing and reducing agents and on systems involving coupled reactions. Miller showed the inadequacy of Luther's classification of coupled reactions, without being able, however, to substitute a clear and workable classification of his own. That particular problem is one which will be solved long before the Centennial celebration.

It was A. A. Noyes, this time in collaboration with Whitney, who wrote the first satisfactory formula for the rate of solution of a solid; but unfortunately their treatment was purely formal and it was left to Nernst to discover that the important factor was the rate of diffusion, both in this case and in many others of reaction velocities in heterogeneous systems. This covers such apparently different things as the rate of solution of iodine in potassium iodide solutions, the action of benzoic acid solutions on magnesia, and the catalytic decomposition of hydrogen peroxide solutions by platinum black.

Catalysis

Great progress has been made in this country in the theory of contact catalysis since the importance of adsorption has been recognized. The very mysterious phenomenon of the poisoning of the catalyst has been cleared up so far as the general theory is concerned, though there is still some question why a given amount of the poison is necessary in any given case rather than some other amount. Langmuir's conception of oriented adsorption has already proved its value and is going to be of increasing importance. In Taylor's laboratory, at Princeton, it has been shown experimentally that nickel splits hydrogen into monatomic, electrically neutral hydrogen, as previously postulated by Langmuir. Bancroft has pointed out that ultra-violet light will do many of the things that a catalyst will do and that consequently the activation of a substance consists fundamentally in the opening of some bond or contravalence, one of the problems then becoming the determination of what bond it is in any given case. This is Baly's hypothesis made a little more definite; it really inaugurates a new organic chemistry, the chemistry of radicals instead of the chemistry of molecules. The statement that reactions are always between ions was never taken seriously because it was known to be inaccurate. It seems probable, however, that most reactions involve activated molecules, the ions being one class of active substances, and the active forms of the organic molecules not necessarily being charged.

Stress has been laid upon the importance of differentiating between the two possible types of contact catalysis. In one case there is an intermediate formation of a definite chemical compound, meaning thereby one which is described by the law of definite and multiple proportions. In the other case there is an intermediate formation of an adsorption complex, or indefinite chemical compound if one prefers that term. Bray believes that these two types merge insensibly, one into the other, and that there are cases which it is impossible to classify under either head. An example of this is the cupric chloride used as a catalyst in the Deacon chlorine process. It is not necessary to assume that a definite oxychloride of copper is produced.

> It is only necessary to assume that an exchange of oxide and chloride ions occurs at various points in the solid cupric chloride lattice. The extent to which such an exchange will occur will obviously depend on experimental conditions, such as oxygen and chlorine concentrations, temperature, and the like. It will only be a fortuitous circumstance if these are such that, on the average, half the chloride ions are replaced by oxide ions; nor, in rapid reactions, can the change be expected to extend much beyond the surface.

Whether one can separate the sheep from the goats with accuracy is a debatable point; but the value of the classification does not depend on that. Everybody will agree that it is desirable to distinguish between animals and plants, even though it is not possible to draw a sharp dividing line. Whewell says that:

> Names of *kinds* of things (*genera*) associate them according to total resemblances, not partial characters. The principle which connects a group of objects in natural history is not a *definition*, but a *type*. Thus we take as the type of the rose family, it may be the common *wild rose;* all species which resemble this flower more than they resemble any other group of species are also *roses* and form one *genus*. All genera which resemble roses more than they resemble any other groups of genera are of the same *family*. And thus the rose family is collected about some one species which is the type or central point of the group.
>
> In such an arrangement, it may readily be conceived that though the nucleus of each group may cohere firmly together, the outskirts of contiguous groups may approach, and may even be intermingled, so that some species may doubtfully adhere to one group or another. Yet this uncertainty does not at all affect the truths which we find ourselves enabled to assert with regard to the general mass of each group. And thus we are taught that there may be very important differences between two groups of objects, although we are unable to tell where the one group ends and the other begins; and that there may be propositions of indisputable truth, in which it is impossible to give unexceptionable definitions in the terms employed.

Taylor believes that the activating atoms (or molecules) of the catalyst usually occupy only a small fraction of the total surface and are those in the surface which are unsaturated—the extra-lattice atoms—which may be held to the mass of the catalyst by perhaps a single bond.

> The X-ray examination of metallic hydrogenation catalysts has shown that these catalysts, even when prepared at low temperatures, possess the definite lattice structure of the crystalline material. A granule of such a catalyst must, therefore, possess, in part, the ordered arrangement of the atoms found in crystalline material. The method of preparation of active material suggests, nevertheless, that the ordered arrangement of the atoms has not been completely attained and that, here and there, on the surface of a partially crystalline material there are groups of atoms in which the process of crystallization is not yet complete.
>
> The atoms in the plane surface of any face of the crystal, e. g , a face-centered cubic crystal of nickel, will be practically saturated by the neighboring metal atoms in three dimensions, with the exception that there will be a certain degree of unsaturation towards the gas phase * * * Atoms in the edges of such a crystal will be one degree less saturated than the atoms in the surface, by reason of the fact that they are surrounded to a less degree by nickel atoms. For this reason they will possess stronger attractive force for impinging atoms. * * * This increased attractive force at an edge will be surpassed by that obtaining at a corner. In the incompletely ordered atoms the attractive force will increase progressively as the degree of saturation by neighboring nickel atoms becomes less and less, until, finally, in atoms which are held to the granule by only one attachment, e g., Ni-Ni, the unsaturation of the metal atom and the attractive force for impinging molecules will become a maximum. The methods of preparation of active catalysts and the activation of inactive masses all tend to produce arrangements of atoms in which these varying characteristics are multiplied.* * * The attractive force of a surface atom may be adequate to retain one molecule, whereas another gas would suffer a practically completely elastic collision. The less saturated atoms in the catalyst surface will be the preferred positions of attachment of catalyst poisons. Hence the varying ratio of adsorption between poisoned and unpoisoned catalyst.

On Taylor's hypothesis, the simultaneous formation of ethylene and acetaldehyde from ethyl alcohol is due to differently oriented adsorption by atoms of the catalyst held differently on the surface or by differently oriented adsorption at different portions of the crystal. Adkins claims that the difference in product is due to a variation in the spacing of the atoms or molecules of the catalysts, and he apparently obtained different alumina catalysts by decomposing different compounds of aluminum. He says:

> On the basis of Dr. Taylor's hypothesis, a slightly unsaturated surface atom might induce one reaction, a more unsaturated one another reaction, etc. That is to say, an atom of a catalyst produces hydrogenation because it exerts a greater (or lesser) force than does one that produces dehydration. It seems to me more reasonable to believe that there are differences in kind rather than of degree of dislocation of the molecule. Instead of there being four or five kinds of catalyst-ethanol compounds or four or five degrees of unsaturation of catalyst atoms, the various reactions are dependent upon the relationship in space of the catalyst atom which are *simultaneously* exerting their attractive forces upon the organic molecule, thereby distorting it in different ways It seems probable that differences in the degree of unsaturation of catalyst atoms as well as the geometrical relationship of these active points, are important factors in catalytic reactions.

Emphasis should be placed on the fact that there are two distinct phases to these catalytic reactions, and that these two phases have apparently no relationship to each other The one phase has to do with *how much* material reacts under a given set of conditions and the other phase has to do with the ratio of the reactions that take place. The first phase may very well have an intimate relationship to the adsorptive capacity of the catalyst. It varies with very slight changes in the method of preparation of the catalyst. In general this behavior of the catalyst is not readily duplicated with different preparations from the same materials. In marked contrast to this is the case of duplication of the characteristics of the second phase; provided the catalyst is made by the same method, i. e., by the ignition of a carbonate, dehydration of a hydroxide, hydrolysis of an alkoxide, etc. Two catalysts made from a butoxide may differ from each other by as much as 100 per cent in the *amount* of material that they will cause to react in unit time, but the proportion of the reactions induced will differ only by a per cent or so. The one characteristic of the catalyst is dependent, I believe, upon the number of active adsorbing centers, the other upon the characteristics of the surface at these active points. The distinctness of these two characteristics of catalysts has never been sufficiently realized.

The Phase Rule

The Cornell laboratory was the first one in this country to do serious work on the phase rule and the Geophysical Laboratory at Washington is a wonderful example of what can be done with the phase rule as an instrument of research. Miller and Kenrick at Toronto University have developed the method of indirect analysis which is most in use in identifying double and basic salts. While we owe much to Heycock and Neville, to Roozeboom, and to Tammann for their work on alloys, there has also been much good work done in this country. Jeffries has worked out what seems to be the best theory of the hardening of duralumin and of steel; and Gillett has done great service in calling attention to the probable bearing of sonims on the fatigue of metals. It is true that the Beilby amorphous-film theory was accepted at one time fairly generally in this country; but we have seen the error of our ways.

Colloid Chemistry

Cameron, at the Bureau of Soils, and Jacques Loeb, at the University of California, did good work on the application of physical chemistry to soils and to biology, respectively. Indeed Loeb's work on the application of physical chemistry to vital phenomena is epoch-making. In both cases the work soon became colloid chemistry. In spite of his brilliancy—or perhaps because of it—Loeb was not able to acquire the new point of view and to the day of his premature death he looked upon colloid chemistry as unmitigated foolishness. Clowes showed that some of Loeb's results on the antagonism of salts could be explained on the assumption that protoplasm acts like an emulsion and that the change from an oil-in-water to a water-in-oil type is favored by certain salts and hindered by others. Some of the cases of antagonism of salts involve osmotic pressure relations rather than emulsification, and Gurchot has shown that salts, alcohols, etc., may cause temporary coagulation or permeability of the semipermeable membrane. This minimizes the difficulty as to the way in which some of the materials get into the cells.

There has been an enormous difference in the lines along which *colloid chemistry* has developed in Europe and in America. This can be seen clearly by comparing the latest edition of Freundlich's "Kapillarchemie" with Bancroft's "Applied Colloid Chemistry." Freundlich's book—stupendous though it is—is essentially a collection of facts. There is no real attempt and not much desire on Freundlich's part to change colloid chemistry from a descriptive to a deductive science.

When discussing contact catalysis, reference was made to Langmuir's theory of oriented adsorption. The similar work on oriented adsorption at the surface of a liquid has created more of a sensation than the other, though it is probably not so important a contribution to science. Bingham's work on plasticity and fluidity is of course colloid chemistry, though he is not overenthusiastic about that side of it because he came into the subject from a study of the fluidity of true solutions.

Electrochemistry

In electrochemistry we start with that part of Gibbs' paper which deals with a reversible cell. In a sense this contains in capsule form about everything which has been done since, though the later work of Helmholtz, Nernst, and others was necessary to show what was in Gibbs and what it meant. There is even to be found in Gibbs the statement that the high chemical potential is at one electrode and the high electrical potential at the other. Goodwin's work on the voltaic cell was done in Germany under Ostwald's direction and should perhaps not be credited to America. Cady showed the effect of the heat of dilution on concentration cells in certain cases and the careful work done in Richards' laboratory proved that this theory accounted for about 75 per cent of the apparent discrepancies. Hulett has done admirable work on standard cells and Lewis obtained the true value of the gas cell to within one one-hundredth of a volt twenty years ago. Ever since then his laboratory has been active in determining free energies by the electrometric method. Lewis was the first to devise a method for measuring the free energy of the alkali metals.

Electrolytic analysis began with Wolcott Gibbs. Although a great deal of the development of this subject was done in Germany, notably in Classen's laboratory, it is to America that we must turn for rapid methods of electrolytic analysis. The University of Pennsylvania laboratory under Edgar F. Smith was for years the headquarters of electrolytic analysis in this country, and it is to Smith that we owe—among so many other things—the ingenious method of determining sodium with a mercury cathode. Electrometric analysis runs back to Behrend in Ostwald's laboratory. Böttger attempted to popularize it; but it was Hildebrand, now of the University of California, who really put the subject across and made the method a regular laboratory one. The definition of pH and the preparation of many indicators we owe to Sörensen of the Carlsberg laboratory in Copenhagen; but Clark and Lubs have done good work in this country in preparing what seems to be the best series of indicators for use over the whole range.

Whitney, now the head of the Research Laboratory of the General Electric Company, was the originator of the electrolytic theory of corrosion, and Walker, of the Massachusetts Institute of Technology, did much to develop it. After a good many vicissitudes, this theory seems now to have weathered the storms and to be the only one worthy of serious consideration so long as we are working under ordinary conditions. Nobody claims that it applies to metals heated in dry air or exposed to an oxyacetylene torch.

It is not possible to claim the electrochemical industries at Niagara Falls for physical chemistry, much as one would like to; because Castner, Acheson, Hall, and Bradley, for instance, were not physical chemists and got no help, so far as we know, from the principles of physical chemistry. On the other hand, the Cottrell process for smoke precipitation and the Betts process for the electrolytic refining of lead are to be credited to physical chemistry, as is also the work on electroplating by Blum, of the Bureau of Standards. The electrolytic restoration of corroded medallions and other objects by Fink of Columbia is a bit of work of which anybody could be proud.

Photochemistry

In photography the Research Laboratory of the Eastman Kodak Company under C. E. K. Mees has been, of course, the center of activity, both in the way of making new sensitizing dyes and in working out problems involving measurement and theory. A most brilliant piece of work is Sheppard's discovery that allyl isothiocyanate or its conversion product, allyl thiocarbamide, is the substance which is responsible primarily for the sensitizing action of gelatin. Somewhat less dramatic are the crystallographic work of Trivelli on the silver bromide grain, the statistical work of Wightman, Trivelli, and Sheppard on the size-frequency distribution of silver halide grains, and the work of Nietz on the electromotive forces of developers. Starting from the premise that any of the photographic developers will reduce unexposed silver bromide when not protected by gelatin, Bancroft worked out a theory of solarization and of development which is based primarily on relative reaction velocities rather than on equilibrium relations. On this basis, selective adsorption and peptization by the developer are of much more importance than the chemical potentials as measured by the electromotive forces.

Over a century ago Grotthuss showed that only that light which is absorbed can produce chemical reaction and that the question whether a photochemical change can occur depends, in many cases, on the presence of a suitable depolarizer. The first of these two propositions was rediscovered by Herschel in England and by Draper in America. It is often called "Draper's law." The second proposition was also forgotten to a great extent and was rediscovered in part by Vogel, in Germany, with his chemical and optical sensitizers. It came fully into its own when it was shown by Bennett, at Cornell, that a copper sulfate solution can be made light-sensitive by the addition of a suitable depolarizer, in this case a solution of phosphorus in ether. A more adequate formulation is that all light which is absorbed raises the chemical potential of the portion of the molecule which absorbs it and thereby makes it less stable. Whether any reaction will take place and what reaction takes place is a question of chemistry. There are, therefore, no chemical rays as such and no oxidizing or reducing rays as such. Since $h\nu$, the Planck constant multiplied by the frequency, has the dimensions of energy, an absorption band in the violet may involve the taking up of more energy than a band in the red, which accounts for the fact that, of two absorption bands, the one corresponding to the shorter wave length and greater frequency is usually the more light-sensitive.

Another important problem in photochemistry is the relation between the amount of light absorbed and the amount of chemical change which occurs—the application of the quantum theory. The lead in this field, so far as America is concerned, is being taken by Taylor, at Princeton. It seems to the outsider as though one should distinguish rather sharply between systems which are in a metastable state, like hydrogen and chlorine, and systems in which the light actually displaces the equilibrium, like oxygen or sulfur trioxide. The interesting cases of so-called chain reactions will probably be found only in the first group.

Porter, at the University of California, has shown that Baly's experiments on the formaldehyde synthesis are by no means conclusive as yet. Spoehr, at Carmel, and Bovie, at Harvard, are studying the photochemistry of the living organism. Langmuir, at Schenectady, has given definite theoretical reasons for rejecting the radiation theory of reaction velocities put forward by W. C. McC. Lewis and by Perrin, while Daniels, at the University of Wisconsin, has made an admirable experimental study of the photochemical decomposition of nitrogen peroxide. Under production of light we have the work of Harvey, at Princeton, on the chemistry of the firefly, and the work, at the Cornell laboratory, by Weiser, Wilkinson, and others on the chemistry both of flame reactions and of cathode ray luminescence.

Exact Measurements

In exact measurements the Harvard laboratories take the lead, whether one considers the atomic weight determinations by Richards and by Baxter, the thermochemical measurements by Richards, the verification of Faraday's law by Richards, or the compressibility measurements by Richards and by Bridgman. Washburn, at the University of Illinois, has developed the technic of measuring electrolytic conductance beyond what anybody else has done, and is now editing the International Critical Tables under the auspices of the National Research Council.

Atomic Structure

Richards has been amply justified in his contention that the atoms cannot consist of incompressible masses; but it is only in the most formal way that one can consider his elastic atoms as standing in any close relation to the modern atom, either of the physicist or of the chemist. Lewis outlined and Langmuir developed what is now known as the octet theory or the Lewis-Langmuir atom. This is sometimes known as the atom of the chemist to differentiate it from the Bohr atom or the atom of the physicist. The essential difference between the two models is that Bohr has the electrons move in orbits around the nuclei of the atoms. Langmuir claims that the facts of stereochemistry prove that the valence forces between atoms act in directions fixed with reference to each other, a point which does not follow obviously from the Bohr model.

In his recent book entitled "Valence," Lewis points out how it is possible, in his opinion, to harmonize the two points of view.

> If we regard as the important thing the orbit as a whole, and not the position of the electron within the orbit, and if each electron is assigned an independent orbit, then we may think of each electron orbit as having a fixed position in space. The average position of the electron in the orbit may be called the position of the electron and will correspond entirely to that fixed position which was assigned in the theory of the static atom.* * * We shall adopt the whole of Bohr's theory in so far as it pertains to a single atom which possesses a single electron. There are no facts of chemistry which are opposed to this part of the theory, and we thus incorporate in the new model all of Bohr's theory which is strictly quantitative. In the case of systems containing more than one nucleus or more than one electron, we shall also assume that the electron possesses orbital motion, for such motion seems to be required to account for the phenomenon of magnetism; and each electron in its orbital motion may be regarded as the equivalent of an elementary magnet or magneton. However, in the case of these complex atoms and molecules we shall not assume that an atomic nucleus is necessarily the center or focus of the orbits. These orbits occupy fixed positions with respect to one another and to the nuclei. When we speak of the position of an electron, we shall refer to the position of the orbit as a whole rather than to the position of the electron within the orbit. With this interpretation, we may state that the change of an electron from one position to another is always accompanied by a finite change of energy. When the positions are such that no change in position of the several parts of the atom will set free energy, we may say that the system is in the most stable state. In a process, which consists merely in the fall of an electron from one position to another more stable position, monochromatic radiant energy is emitted, and the frequency of this radiation multiplied by *h*, the Planck constant, is equal to the difference in the energy of the system between two states. The electrons of an atom are arranged about the nucleus in concentric shells. The electrons of the outermost shell are spoken of as valence electrons. The valence shell of a free (uncombined) atom never contains more than *eight electrons*. The remainder of the atom, which includes the nucleus and the inner shells, is called the kernel. In the case of the gases it is customary to consider that there is no valence shell and that the whole atom is the kernel.

Lewis has now modified somewhat his conception of what he called the "group of eight" and which Langmuir called the "octet."

> The new theory, *which includes the possibility of complete ionization as a special case*, may be given definite expression as follows: Two atoms may conform to the rule of eight or the octet rule, not only by the transfer of electrons from one atom to another, but also by sharing one or more pairs of electrons. These electrons which are held in common by two atoms may be considered to belong to the outer shells of both atoms.
>
> The discovery that those electrons which are held jointly by two atoms always occur in pairs led to the realization that the "rule of two" is even more fundamental than the "rule of eight." We see at the beginning of the periodic table that helium, with its pair of electrons, has the same qualities of stability that characterize the remaining rare gases which possess outer octets. Hydrogen may form hydrogen ion with no electrons, it may form hydride ion by adding one electron and thus completing the stable pair, or finally two hydrogen atoms may unite to form the hydrogen molecule, in which each atom shares with the other this stable pair of electrons. I called particular attention to the remarkable fact that when we count up the electrons which are comprised in the valence shells of various types of molecules, we find that of some hundred thousand known substances all but a handful contain an even number of such electrons. It is, therefore, an almost universal rule that the number of valence electrons in the molecule is a multiple of two.

Crystal Structure

Hull and Davey, at Schenectady, and Wyckoff, at the Geophysical Laboratory, have been active in the field of crystal structure.

Radioactivity

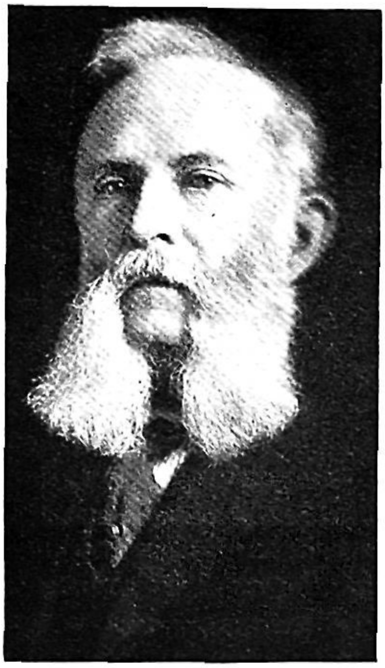
In the field of radioactivity we have the methods of extracting radium from the Colorado ores which were worked out by Parsons and Moore, the discovery of ionium by Boltwood, and the radioactive measurements of Lind. Boltwood mixed ionium and thorium, and showed that the mixture could not then be separated. This was an important preliminary step to the understanding of the behavior of isotopes. Harkins has got actual results on the fractionation of isotopes, and Kendall has developed a method which looks promising. The occurrence of helium in natural gas was discovered by Cady, and the final method of extraction and purification is due to Moore.

Thermodynamics

In thermodynamics Gibbs is, of course, still in a class by himself; but that does not mean that others have not done good work. Trevor set himself the task of presenting chemical thermodynamics in a more accurate and more polished form. This is a dangerous thing to do because it is likely to lead, as it did in his case, to the interest in mathematics superseding the interest in chemistry. Richards just missed deducing the third law of thermodynamics. Washburn introduced the conception of thermodynamic environment; but never carried it beyond the formal stage. Miller has specialized in the zeta function of Gibbs. As has been stated, Lewis developed the conception of activity, which does not seem to be an improvement on Gibbs; he worked out methods of measuring free energy; and, in conjunction with Randall, has written a successful book on "Thermodynamics and the Free Energy of Chemical Substances." Whether it was wise or helpful to break away as completely as he did from the notation of Gibbs is a question which various people have already answered differently. The work of Lewis on relativity is rather out of the field of physical chemistry at present. Among Tolman's contributions are the determination of the mass of the electric carrier in metals and papers on statistical mechanics applied to chemical kinetics and on the similitude principle. Langmuir's work on electron emission, on surface tension, on contact catalysis, and on molecular distribution is extremely brilliant.

Applications

In the applied field the tungsten lamp and the Coolidge tube are two of the striking achievements of the physical chemist. For that matter the whole output of the Research Laboratory of the



Harris & Ewing

William F. Hillebrand
(1853–1925)
President 1906

Marston T. Bogert
(1868–   )
President 1907, 1908

Willis R. Whitney
(1868–   )
President 1909

Wilder D. Bancroft
(1867–   )
President 1910

General Electric Company is to be credited in the last analysis to W. R. Whitney and consequently to physical chemistry.

Journal of Physical Chemistry

The *Journal of Physical Chemistry* was started in 1896 and is now in its thirtieth year. Through the support of the Chemical Foundation it has become an international journal for the English-speaking peoples and is now published under the auspices of the AMERICAN CHEMICAL SOCIETY, the Chemical Society (London), and the Faraday Society. Even this outlet does not relieve appreciably the strain on the *Journal of the American Chemical Society.*

Future Problems

The future of physical chemistry calls for a few words, because we cannot gauge the progress satisfactorily unless we know something about the goal. One of the leading physical chemists of America has said:

> Physical chemistry exists no longer. The men who have been called physical chemists have developed a large number of useful methods by which the concrete problems of inorganic chemistry, organic chemistry, biochemistry, and technical chemistry may be attacked. As the applications of these methods grow more numerous, it becomes increasingly difficult to adhere to our older classification.

According to this, physical chemistry is a technic and not a point of view. The other side is that the physical chemistry of dilute solutions is not in good shape so long as it is possible to speak seriously about sodium chloride being 100 per cent polarized or ionized, 85 per cent electrolytically dissociated, and 60 per cent thermodynamically dissociated. We have made no serious attempt as yet to tackle the theory of concentrated solutions, chiefly because we have assumed that it must be very much more difficult than the theory of dilute solutions. In a sense this is true, because some of the disturbing factors become negligible in very dilute solutions. On the other hand, the place to study these disturbing factors is in the concentrated solutions where their effect is large enough to make the form of the function easy to find.

No one disputes that we are very far from being clear as to the physical chemistry of non-aqueous solvents. We are only just working out a theory of colloid chemistry and it will be a good while before we can say that we really understand about dyeing, paper, leather, paints, rubber, pottery, cement, etc. While the organic chemist does make conductivity determinations and molecular weight measurements, and does study reaction velocities occasionally, it would be a bold man who would claim that anything more than a beginning had been made in the application of physical chemistry to organic chemistry.

There are a number of important developments in physical chemistry which some of us should live to see. We need the development of a more exact thermodynamical theory of chemical statics and dynamics, which will put the electrolytic dissociation theory, the theory of non-aqueous solutions, and the theory of concentrated solutions on a satisfactory basis. This will include a quantitative recognition of the effect of changing the degree of polymerization of the solvent.

We need an extension of Loeb's work on the application of chemistry to vital phenomena and we need, above all, a knowledge of the chemical processes as they go on in the plant and animal. We are not yet really certain of the way in which carbon dioxide is assimilated and one gets no answer if one asks how a shellfish puts bromine into the compound from which we get Tyrian purple.

We are only just starting on a scientific study of photochemistry, and we know almost nothing as yet about the photosynthesis of organic compounds. In the absorption spectrum of any given substance, we must determine which lines or bands belong to the molecule and to what parts of the molecule they belong. If we can then develop an efficient method of producing an intense light of any desired wave length, we have the possibility of an entirely new organic chemistry with perhaps 100 per cent yields. Of course one does not expect the organic chemist to believe this. I am not sure that I believe it myself; but it is a possibility and a fascinating one.

Except for atomic spectra we have made very little progress in the theory of chemiluminescence, though the production of cold light is a problem that we ought to be able to solve and that we probably shall solve as soon as somebody tackles it both systematically and intelligently.

We know that chemical reaction velocity is probably directly proportional to the difference in chemical potential and inversely proportional to the chemical resistance; but we have not yet started on the question of what we mean by chemical resistance and consequently we do not know what really determines the speed of a reaction. We have been satisfied *hitherto with a formulation of* the laws of chemical kinetics. Now that we are able to calculate the equilibrium constants with some degree of accuracy from the third law of thermodynamics, we must begin the study of the reaction velocity constants, of which we can now predict the ratio.

We must develop a theory of contact catalysis which will enable us to prophesy what catalytic agent will give us a particular result. In the recent synthesis of methanol, we could predict that high pressure would be helpful; but nobody could have said in advance that zinc oxide would be the best catalyst. They had to try one hydrogenating catalyst after another until the right one was found —a slow and unsatisfactory procedure in general. Since the contact catalytic agent activates substances in most cases by opening some bond, we need a study of the organic radicals thus produced, so that we may have a real knowledge of the intermediate steps in organic reactions. The question of contact catalysis and overvoltage in electrochemistry is also one of great interest.

We need two institutes of colloid chemistry. One is already advocated by the Committee on Colloid Chemistry of the National Research Council; it would deal with pure science, would develop the technic, and would render invaluable service by applying colloid chemistry in biology and medicine. The other should deal with the applications to the industries and should develop the scientific foundations of the so-called colloid chemistry industries, such as textiles, paper, leather, dyeing, paints and varnishes, rubber, pottery, cement, photography, etc. At present the practice is far ahead of the theory in these industries. Judging from the past, we are justified in concluding that bringing the theory up to or beyond the present state of the art would be followed very soon by distinct industrial advances.

The real work on the structure of the atom only dates back a few years and we can look forward with confidence to very great advances in this field within the next few years. While most of the work hitherto has been done by physicists, the development will soon reach a point where it will become more and more physical chemistry. That has been the universal experience, as shown strikingly in the theory of the voltaic cell and in the work on electrolytic conduction, to cite two instances out of many.

Another thing that the physical chemist must do, because he is apparently the one with the pioneering spirit, is to develop the borderlands between physical chemistry and the other sciences, such as biology, geology, physics, medicine, engineering, psychology, etc. It should be the aim of all chemists to have chemistry take its place as the fundamental science and that can only be done by and through the physical chemist. The idea that there is no future for physical chemistry is very far from the truth.

CHAPTER VIII

INORGANIC CHEMISTRY

BY JAMES LEWIS HOWE

Introduction

The close of the third quarter of the nineteenth century found inorganic chemistry at its lowest ebb. Under the leadership of Hofmann, organic chemistry had well-nigh preëmpted the whole field of chemistry. Wöhler was the last living representative of those who had devoted their lives largely to the development of inorganic chemistry, and he was an old man, no longer active in the laboratory. In truth, inorganic chemistry had progressed about as far as it could with the tools at hand. The good behavior of the carbon atom, holding the atoms steady in the molecule in the position in which they had been placed, with its four stable valences—not too many for easy handling, yet sufficient to afford a reasonable variety—and, above all, its willingness "to combine with itself indefinitely without affecting the stability of the molecule," all these contributed to hold the attention of chemists, enabling them to prepare a multiplicity of definite new compounds. The organic compounds and reactions were systematized and made the basis of chemical theory, and many of the compounds found application in the dyestuff and other industries.

In this country there had been a few workers along inorganic lines, such as Charles Upham Shepard, who had done much to develop the phosphate beds of South Carolina; T. Sterry Hunt, who had extended the work of Gerhardt, but whose views were often erratic; J. Lawrence Smith, whose particular interest was in minerals and meteorites and their analysis, and who perfected many analytical procedures; Josiah Parsons Cooke, who had been one of the first to grasp the whole trend of what was then modern chemistry. But these men had none who could properly be called their successors, nor was there incentive or training for the development of inorganic chemists.

A half-century ago there was practically no graduate work done in chemistry in this country. There were good teachers and good students, but the chemistry of that day was "made in Germany," and thither went the American students, largely to Göttingen for the sake of its old reputation under Wöhler, or Berlin to work with Hofmann, or Bonn with Kekulé, or Würzburg for analytical work with Fresenius, or Heidelberg, perhaps for a good time, for Bunsen's work was practically over. With the exception of those at Würzburg, by far the largest number of theses were in organic chemistry, and little interest was paid to inorganic research. As a result, few American chemists of the period worked on inorganic problems. A decade later and the scene had changed, but not directly to the advantage of inorganic chemistry. Kolbe had been succeeded at Leipzig by Ostwald, and a new field of chemistry opened—that of physical chemistry. From now on research problems were offered in abundance, and the then younger generation of American chemists was not slow to take them up. Johns Hopkins University had been founded, other well-equipped graduate departments in chemistry were established, and in them all research in physical chemistry was dominant, in spite of the hold organic chemistry had on the older teachers.

But if physical chemistry was opening a field of its own, it was also furnishing a most valuable tool to the inorganic chemist, and it was soon recognized that practically all of the older work in inorganic chemistry must be repeated in the light of the newer theories. Furthermore, the periodic system of the elements, as set forth by Mendeléef and Lothar Meyer, was gradually becoming recognized as a foundation principle, and it was seen that from this standpoint the rarest and least investigated of the elements was as important as the best known, or even as carbon with its myriad compounds. It was soon realized that inorganic chemistry offered a limitless field of problems, and the most that a single worker or group of workers could hope to accomplish seemed insignificant when viewed in comparison with all that must be done before any far-reaching generalizations could be gained.

For this reason, there have been few systematic researches along purely inorganic lines; it has been a bit here and a bit there, but in the aggregate making no small contribution to our knowledge of inorganic chemistry. There have been three lines of work, however, in which American chemists have done much to advance our whole knowledge of chemistry, though the work has been done almost wholly in the inorganic field.

Double and Complex Salts

The first of these lines concerns double and complex salts. The first worker in this field was Wolcott Gibbs who, before the period we are considering, had done much work on the compounds of tungstic and molybdic acids. He early recognized the complexity of the problem, which had, indeed, been suggested long before by Berzelius and later by Marignac, and found it necessary at the start to go into a long and detailed study of the tungstates and molybdates of the alkalies and other bases. Regarding the alkaline tungstates, he states in his opening paper some of his difficulties: they are numerous and unusually complex; salts of essentially different formulas approach so closely in percentage composition that the differences lie very near the unavoidable errors of analysis; almost all are markedly efflorescent, and the salts of different series often agree closely in chemical properties; many are decomposed by hot water, yielding two or more different salts in solution. Of course these difficulties are a commonplace to workers in this field today, but must have been well-nigh overpowering to a pioneer. It was rather the custom of that day to solve a problem if the solution was easily reached, but if it proved difficult, to lay it aside and take another; there were plenty of problems easy of solution. It is to Dr. Gibbs' credit that he kept at his problem and vastly widened our knowledge of complex salts, even if many of the conclusions he reached are not valid in the light of modern methods. From the simple tungstates and molybdates he was led to the phospho- and arseno-tungstates and molybdates, and then to others, till in his final paper he sets forth no less than thirty-five series of complex salts in addition to the seven which had been earlier described by Struve and Parmentier, all containing MoO_3 or WO_3, together with some of the following oxides: P_2O_5, As_2O_5, V_2O_5, Sb_2O_5; VO_2, SnO_2; P_2O_3, (H_3PO_2), (HPO_3), As_2O_3, Sb_2O_3. He also points out the possibility of further classes of salts in which the group $PtCl_2$ takes the place of O, or $(2PtCl_3)'''$ the place of 3O. Of these, $(HO)_3P(PtCl_2)$ is the simplest member. The Cl of the $PtCl_2$ may be replaced by Br, and his experiments showed that similar compounds are formed with all the platinum metals except rhodium, which he was unable to test as he could get no rhodium. Among the salts of these series prepared by Gibbs were $5(NH_4)_2O.As_2O_3.3(As_2O_3.2PtO).7H_2O$ and $K_2O.(As_2O_3.2PtCl_2).2H_2O$. This work opens up an enormous field which no one has entered, and of which Gibbs only skirted the edge; it would offer today great possibilities to the chemist equipped with X-ray spectroscopy.

The investigations of Gibbs on the complex tungstates and molybdates were followed by the work of Edgar F. Smith, alone and with Allen Rogers. They much enlarged the field, bringing in many new oxides, such as tantalic and columbic acids, as well as the oxides of the rare earths. While Gibbs never had more than three different acids acting as a complex anion, they prepared many compounds with four. An example of the complexity of some of these salts is shown by the formula $82(NH_4)_2O.12P_2O_5.3As_2O_5.5V_2O_5.201WO_3.567H_2O$, a salt crystallizing in regular octahedra. These compounds certainly offer an interesting field for X-ray analysis.

Meanwhile Ira Remsen had been taking up the subject of the double halides, of which some, such as the chloroplatinates and fluosilicates, were very familiar salts. He discussed them from a theoretical standpoint, bringing out his theory of the double halide atom and thereby seeking to clear up the valence difficulty. Under the old view, these double halides were "molecular" compounds; K_2PtCl_6 was a "molecular" compound between two potassium chloride molecules and one of platinum chloride. In the case of many of the double salts this was fairly satisfactory, since the double salts were resolved into their simpler components in solution, but in others, such as those mentioned, the groups $PtCl_6$ and SiF_6 were far too stable for chemists to be content with any of the earlier explanations. The same, of course, was true of "water of crystallization." According to Remsen's view, the halogen atoms are in part in pairs, these pairs functioning like oxygen as a bivalent element. In many cases the halogen double salts were wholly analogous to the corresponding oxygen salts. Although this conception has been largely superseded, it was an important generalization, and led to much advancement in our knowledge of this class of compounds. While quite a number of contributions to the subject were made by the pupils of Remsen, the most important developments on double halides were made by H. L. Wells, assisted on the crystallographical side by S. L. Penfield. Wells collected the literature of the subject and prepared a systematic arrangement of all known double halides, thereby furnishing a starting point for all future investigators. He and his students also prepared large numbers of new salts, among them the chloroantimonates, in which the antimony is quadrivalent. The work of Remsen, and more particularly that of Wells, laid the foundations and furnishes no inconsiderable portion of the material used by Werner in developing his coördination theory, while the work of Gibbs led to that of A. Rosenheim in the application of Werner's theory to the tungstic and molybdic acid complexes.

Since that time further work on double and complex salts has been carried on by H. W. Foote and others. One interesting phase, which dates from an earlier period, is in connection with mixed haloplatinates. One of the first papers of importance in THE JOURNAL was that of Lucius Pitkin, who prepared the whole series of mixed potassium chlorobromoplatinates, from K_2PtCl_5Br to $K_2PtClBr_5$. With the development of the methods of physical chemistry, it appeared that this series was in reality made up of solid solutions, and possibly none of the members was a chemical individual. Charles H. Herty, however, later showed that certain mixed haloplatinates could be prepared as definite compounds. In the light of modern methods it has been shown that a great many inorganic compounds described in the earlier chemical literature are not valid, and a repetition of much of this work has revealed that it needs to be again gone over from a modern standpoint.

Liquid Ammonia Solutions

A second line of work, largely if not wholly American in its development, is that of E. C. Franklin on liquid ammonia solutions. Although not so extensive as that on double salts, it is more far-reaching in its implications. Until this work by Franklin, practically all chemistry and chemical theory, except that at high temperatures, had been confined to elements and compounds in relation to oxygen and water. This was inevitable when one considers the extreme difficulty of completely removing water from any sphere of reaction. Starting with reactions in liquid ammonia as a solvent, Franklin has gradually unfolded the conception of a chemistry in which nitrogen plays the familiar part of oxygen or, more accurately, ammonia the part of water, the amino group, NH_2, that of the hydroxyl, and the imino group, NH, that of oxygen. In this chemistry appear ammono acids, ammono bases, and ammono salts, and many of the reactions are wholly analogous to those of our ordinary oxy acids, bases, and salts. Of course this is a low-temperature chemistry, since liquid ammonia is the solvent, and this has entailed manipulative difficulties which would have completely deterred many experimenters; but Franklin has surmounted them, often most ingeniously, and has opened a new field, of which the surface has as yet hardly been scratched. The present state of the work is much like that of general inorganic chemistry a hundred years ago. For the most part only relatively simple compounds have been prepared, but there is evidence of complexity, possibly as great as that in water chemistry. But the story does not stop here, as Franklin has shown in his recent presidential address before the AMERICAN CHEMICAL SOCIETY. The possibilities of a sulfur or thio chemistry open up. We have already knowledge of a considerable number of thio acids, bases, and salts, but these include only such compounds as are relatively stable toward water. Replacing water by liquid hydrogen sulfide, the new field appears. Toward many of our familiar compounds, especially salts, liquid hydrogen sulfide is not an ionizing agent, but it may have a chemistry of its own, as is more than hinted at in the recent and very promising work of J. A. Wilkinson. A halo chemistry has already been recognized, but here, too, only in relation to water; liquid hydrogen chloride is also not an ionizing agent, but perhaps only because we have not found the proper conditions. Franklin suggests that there may even be a carbon chemistry, very different from our present conceptions of organic chemistry, and independent of oxygen. From this standpoint alone it may be that inorganic chemistry, as we know it, is only in its infancy.

All this is somewhat connected with the use of liquids other than water as solvents and ionizing agents. Victor Lenher has worked with selenyl chloride, SeO_2Cl_2, as a solvent; H. B. North with sulfuryl chloride, SO_2Cl_2, as well as with thionyl chloride, $SOCl_2$; F. E. Brown with vanadyl chloride, $VOCl_3$. H. A. Curtis has used isoamyl alcohol; and Davidson absolute sulfuric acid. The work of H. S. Fry and A. W. Browne, and C. A. Kraus should also be noted. Browne has used liquid hydrazine as a solvent, while Kraus is working with metals, as well as with organic compounds, in liquid ammonia. All this shows what a field stands before the *inorganic chemist, waiting for exploration.*

Solvates

The third line of work by American chemists leading to important generalizations is that of Harry C. Jones on solvates. While the work of Jones would probably be claimed by the physical chemists, the conclusions drawn belong in the field of inorganic chemistry. At a time when the physical chemists were busying themselves with dilute solutions, progressing as nearly as conditions would allow to ideal solutions, that is, solutions of infinite dilution, Jones began his attack on actual solutions, such as those in which our ordinary chemical reactions are carried out, approaching the saturated solution as a goal. It quickly appeared that such solutions were far from obeying any of the theoretical laws of solution, and Jones set himself the task of finding out why. One factor soon appeared, that the water of his solutions was disappearing as solvent water in an unaccountable way; the solutions were acting as if more concentrated than they really were. Further experimentation showed a relation between this missing water and the "water of crystallization" of the salt. It required prolonged research to prove, as Jones and his pupils did, from many different standpoints, that both salts and ions exist as hydrates in solution; indeed, that in a saturated solution of a hydrate, the solid phase is actually in equilibrium with a saturated solution of the hydrate itself, rather than with some of its constituents. An analogous condition applies to solvents other than water, and the term "solvate" has been well coined to apply to the condition of many solutes which exist in solution already combined with more or less of the solvent. This has furnished an important contribution to our knowledge of solutions, and has yet an important part to play in assisting X-ray spectroscopy in the study of crystal formation from solution.

Early Miscellaneous Investigations

Turning back to the earlier part of the half-century under review, we find that most of the contributions to inorganic chemistry were of the nature of pieces of work which a busy college professor could find time to carry out with his own hands, possibly with the aid of some assistant; the period of graduate students had not yet arrived, and the limitations on research were great.

PHOTOCHEMISTRY.—M. Carey Lea accomplished a notable piece of work on the photochemistry of silver salts and on colloidal silver, and, with the work of Romeyn Hitchcock and of Spencer B. Newbury, the way was paved for the later marvelous developments of photography. These were the pioneers.

ATOMIC WEIGHTS.—Frank W. Clarke, who had just begun his career by studying the iodates and selenocyanates, a number of other double salts, and the action of phosphorus on platinum and iridium, was soon attracted by atomic weight calculations and the molecular structure of the silicates. It is with these last two we always associate him. The subject of atomic weights will also be thought of in connection with the name of Theodore Richards, not to omit J. W. Mallet, E. W. Morley, W. A. Noyes, Edgar F. Smith, and G. P. Baxter, but this belongs to the field of analytical chemistry.

GEOCHEMISTRY.—In his work upon the silicates, Clarke undertook to carry over the ideas of structural chemistry, on which organic chemistry had been built, into the realm of inorganic chemistry, and particularly to apply these ideas of structure to the silicates. This brought out unexpected relations between minerals and enabled a systematization, otherwise impossible, of these compounds. Although structural formulas mean less and less to us today in inorganic compounds, they served an indispensable purpose in the development of our theories, while waiting for the revelations of X-ray spectroscopy. In this development the work of Clarke had a most important part. Of more permanent value has been his geochemical work, which is wholly in the field of the inorganic; especially in his calculations of the relative abundance of the elements on the earth and the gross make-up of its outer portion. Another contribution of Clarke to inorganic chemistry—one unmentioned in the books—is his habit of throwing out pregnant suggestions to those in close contact with him. I suspect that many a piece of work with which the name of Clarke is never associated was in reality inspired by him.

WATER OF CRYSTALLIZATION.—In these pre-Wernerian days there was naturally much speculation as to water of crystallization, and how it could be reconciled with the then current valence theories. Even in this period it was recognized that oxygen might possibly be quadrivalent—incidentally one of the facts that chemists have had most difficulty in swallowing—and A. S. Cushman suggested a structure for the hydrated chlorides, in which the chlorine might be directly attached to the metal, or to the oxygen of the water, which itself, in turn, was attached to the metal or to the oxygen of another water molecule. This accounted very neatly for the fact that only a part of the water was lost at lower temperatures, but F. A. Gooch and D. A. Kreider, working on the loss of water in atmospheres of hydrochloric acid gas, came near applying the methods of modern physical chemistry, and rendered Cushman's ideas improbable. Nevertheless, this work was a contribution to the development of modern theories, and incidentally had a rather direct bearing on the problem of obtaining anhydrous chlorides, especially of aluminum and magnesium. The dehydration of crystalline salts was also studied in this period by T. W. Richards, and by J. W. Mallet.

Although much of Mallet's work was taken up with the chemistry of minerals, he also worked on the dehydration of alums and on nitrogen iodide. This last was a precursor of the later work of W. A. Noyes on the chloride of nitrogen and its reactions. A. R. Leeds was interesting himself largely with the mechanism of oxidation, which included studies of ozone and hydrogen peroxide, and what Leeds called "the atomation of oxygen." One of his papers, as well as an early paper by Remsen, was on the oxidation of carbon monoxide, a topic which was later to come to the front in connection with masks for poison gases, and on which much has recently been done by W. C. Bray and by A. F. Berton in connection with various catalysts.

THE WORK OF EDGAR F. SMITH.—Of those who were beginning activities at this period none was more versatile than Edgar F. Smith, to whose work on the salts of complex acids allusion has already been made. Although his attention was early devoted to analytical chemistry and especially drawn to the possibilities of electrolytic analysis, the development of which will doubtless be considered his *magnum opus*, his studies of many of the less common elements greatly enlarged our knowledge. This was particularly the case in his work on tantalum and columbium. His studies of the action of hydrogen chloride on such salts as selenates, tellurates, and phosphates, and of the chloride of sulfur on substances, led to important developments in the analysis of numerous minerals, and this, in turn, to many valuable atomic weight determinations. Much of his work in pure inorganic research has, in the hands of others, led to important applications in other fields. It is interesting that in recent years Smith has devoted himself to historical chemistry, and has brought to light so much of worth accomplished by early American chemists. Not the least valuable of Smith's work is the stimulus given to those working under and with him. Of these, none has done more to contribute to our knowledge of inorganic chemistry than Victor Lenher. Beginning nearly three decades ago with the study of selenium and tellurium, he is continuing this work at the present time. Of particular interest is his work on selenyl chloride, SeO_2Cl_2, which not only shows peculiar reactions as a solvent, but is apparently a useful reagent for the separation of molybdenum from tungsten and columbium from tantalum, and may possibly be capable of industrial applications. This latest work is on selenium monochloride, which shows itself to be a typical acid chloride and a strong chlorinating agent.

Hydrated Silica

Along quite a different line Lenher has made a valuable contribution to inorganic chemistry in the study of hydrated silica. It has long been a question how far hydroxides are to be considered as chemical individuals and how far as merely hydrated oxides. In the case of the silicates, we have derivatives of a great number of silicic acids, but do any of these acids actually exist? Thirty years ago T. H. Norton prepared a hydrated silica having the formula of orthosilicic acid, H_4SiO_4. This was obtained by squeezing the water out of a silica gel, and drying under constant conditions. More recently Lenher has followed the same procedure, but used far greater pressures. While Norton used perhaps 100 kilos per square inch, Lenher carried his pressures to considerably over 100 tons per square inch. Under these conditions far more water is removed, but there still remains water corresponding to about $H_2O.2SiO_2$. A portion of this water is removable in the presence of phosphorus pentoxide. The amount of water in the gel appears to be a function of the pressure, and it would seem extremely doubtful that any definite hydrate of silica exists. It is a natural inference that the same is true of other gelatinous hydrates. The silica gel has also been studied by W. A. Patrick, both as to its heat of wetting and also as to the possibility of displacing the water by organic liquids, as alcohol and benzene. He has found, contrary to earlier observations, that not all the water can be displaced, and the nature of this small amount of residual water, so difficult to drive off at any but high temperatures, still remains to be determined. All of this has also a very important practical and industrial application in the adsorptive power of the dry silica gel for gases, on which much work has been done by Patrick. Lenher has also thrown light, not only on the solubility of water in silica, but on the solubility of silica in water. It is well known that practically all natural waters contain silica in solution, at least to the extent of a few parts per million. By grinding quartz, as well as other minerals, in a ball mill it was found possible to carry notable quantities of silica into solution, and this solution is colloidal. It would thus seem that fine grinding is responsible for the silica content of natural waters. This recalls the earlier work of Cushman on the formation of plastic clays by ball-mill grinding of silicates and even of glass. Lenher also found that the solubility of silica increased rapidly with the temperature. Here would seem to open a large field for investigation in geochemistry.

The Rare Earths

A subject that has attracted the attention of many workers abroad also owes much to American chemists in its development, the subject of the rare earths. More than forty years ago J. Lawrence Smith proposed the oxalates as suitable salts for effecting the separation of these elements, a problem which is by far the most difficult of its type in the whole range of chemistry. At about the same period T. H. Norton did considerable work on cerium. It was reserved for the development of the Welsbach mantle to furnish an abundance of what had been rare raw material. Thanks to the interest of Waldron Shapleigh and later of H. S. Miner in rare earth research, the great mass of by-product earths from which the thorium had been extracted became available to chemists. It is nearly a score of years since Charles James began his work; at about the same time Lenher, and shortly after L. M. Dennis, tackled the intricate problems associated with the separation of these elements which resemble each other so closely. James has continued his researches down to the present time and has made large contributions to our knowledge of the subject. His first success was in the use of the bromates for separation, and for the first time thulium was prepared in a pure condition and in considerable quantities. James later, in addition to the more commonly used salts, called the sebacates and cacodylates to his aid. In addition to preparing the earths in pure form, he has studied their properties and in a large number of cases determined the atomic weight. Lenher studied especially the yttrium earths and has used the succinates and the stearates for separation. Dennis made use of the picrates and also studied the electrolytic separation of the earths. Somewhat later, work on the rare earths was taken up by C. W. Balke and by B. S. Hopkins, who have studied particularly dysprosium and holmium, and very recently Hopkins, armed with the methods of X-ray analysis, has announced the discovery of the lines of "61," the missing element for which many chemists abroad and L. F. Yntema in this country had been diligently searching. This element, called "illinium" from the university and state in which it was discovered, is the second to be associated by name with America. May its fortune be better than that of the first, columbium, which long masquerading under the name "niobium" nearly lost its patriotic birthright! The story of the hunt for "61" is most interestingly told in the June number of THE JOURNAL,[1] and is a fine illustration of modern scientific methods of research.

Other Rare Elements

Two other elements will always be associated with American chemists, zirconium, to the knowledge of which F. P. Venable has contributed so much, and beryllium, to which C. L. Parsons devoted his time until called to develop the AMERICAN CHEMICAL SOCIETY. To Parsons also belongs the credit of fastening the name

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[1] *J. Am Chem Soc*, **48**, 1594 (1926)

"beryllium" to the element, earlier and more commonly known as glucinum. While the association of the name of Venable with zirconium is known to all chemists, it is not so generally known that to Venable belongs the credit of the discovery of calcium carbide in electric-furnace products and the production of acetylene by its action on water. It was while the poles of a large dynamo at Spray, North Carolina, were being stuck into every conceivable mixture, that in one of the fused masses Venable discovered a brown crystalline substance which gave him a combustible gas on dropping into water. Simple enough in the retrospect, but in that day not every one, not even every chemist, would have had the knowledge to follow up the phenomenon. Although the work of the electric furnace belongs in another field, this review of inorganic chemistry would be incomplete without at least a mention of the early work of E. H. and A. H. Cowles and C. F. Mabery on the reduction of the oxides of boron and silicon, aluminum and other metals, by carbon in the electric furnace, and the work of G. De Chalmot on silicides and carbides.

We have already alluded to the work of L. M. Dennis on the rare earths. His earliest research was on the chlorides and hydroxides of cerium and the resolution of didymium, but his attention was soon attracted by the newly discovered hydrazoic acid, HN_3, the nature and reactions of which he and his students have done so much to elucidate. This has been extended by Dennis and A. W. Browne and J. W. Turrentine to the study of hydrazine and its oxidation, and by Browne to azido (N_3) derivatives of thiocarbonic acid, which promise further very interesting results. Some ten years ago Dennis took up the investigation of gallium, and to him, as well as to P. E. Browning, we owe a much fuller knowledge of this rather rare element. More recently Dennis was fortunate enough to find germanium present in certain zinc-ore residues, they running at times as high as 0.25 per cent germanium oxide, and he has been able to work with quantities of the metal hardly dreamed of by Winkler. Up to this time germanium had been the rarest of the metals, our knowledge of it being confined to the work of its discoverer, Clemens Winkler, on a small amount obtained from Freiberg argyrodite, and to some non-chemical work of Viktor Goldschmidt on quite a considerable quantity of argyrodite from Bolivia, which had been received by the Oslo University as "Fahlerz." Dennis extracted the element in quantity and has been enabled to make a much more complete study of its properties and compounds than had Winkler with his small amount of material. The most interesting part of his work is now in progress and concerns the hydrogen compounds of germanium, in which germanium shows a striking analogy to carbon. Monogermane (GeH_4), digermane, and trigermane have already been prepared and the end is not yet. Work on germanium has also been carried on by J. H. Müller (Is there any rare element that has not been studied in the laboratories of Edgar F. Smith?) on the allotropy of germanium dioxide and on the recognition of germanium by Marsh's arsenic test, in which germane functions as arsine. He has also found that fluorgermanic acid is not precipitated by hydrogen sulfide, which enables the purification of germanium from arsenic—a difficult problem. Dennis has further made some interesting experiments with germanium glasses. Mention should also be made of Dennis' unsuccessful search for eka-cesium, in which chlorides of the alkalies of pollucite were submitted to an exhaustive fractionation; but the end fractions showed no spectroscopic evidence of a new element.

Allusion has been made to the studies of W. A. Noyes on the chlorides of nitrogen. The composition of the very explosive iodide of nitrogen had long been a matter of discussion but was practically cleared up by the work of H. P. Cady and of F. D. Chattaway nearly thirty years ago. The chloride of nitrogen is far more unstable, but has been successfully worked on by Noyes for many years, especially in connection with its organic derivatives Some of these chloramines have acquired great importance as antiseptics. Considering from its oxidizing power that the chlorine in NCl_3 is positive and the nitrogen is negative, Noyes has tried to prepare an isomer in which the nitrogen is positive and the chlorine negative, but has not thus far succeeded. Mention of Dr. Cady recalls his work in 1907 on the analysis of the natural gas from Kansas wells. In one of these, the Dexter well in southern Kansas, quite an appreciable amount of helium was found. This led to an examination of other wells from the helium standpoint, and it was found that helium was present, at least in very small amounts, in practically all the wells of Kansas, though the quantity was variable. There was so much geographical regularity in its occurrence that Cady prepared an isohelium map for the state. No one could have then foreseen that little more than a decade later this work would have led to the use of helium in balloons. A chance remark of Sir William Ramsay that helium would be an ideal gas for the inflation of military balloons; a still hunt, based on Cady's work, for helium-richer wells; cylinders of compressed helium ready for shipment to the front; and had the Armistice been a few weeks delayed it would have been a surprised enemy at the failure of incendiary bullets to ignite the observation balloons—and all as the result of pure inorganic research.

Catalysis

Another line of research in which pure science and practical application are closely tied together is the work on the catalytic oxidation of carbon monoxide, already touched on in connection with the early work of Leeds. The more modern chapter originated in the effort to make gas masks which would absorb carbon monoxide, but it was soon recognized that from an industrial standpoint it was even more important that there should be some way in which to remove the last traces of carbon monoxide from the gases used in the Haber process of making synthetic ammonia from a mixture of hydrogen and nitrogen. The source of the hydrogen is generally water gas, and whereas the carbon dioxide and most of the carbon monoxide are readily removed, a minute trace of this latter gas is very poisonous to the catalyst. As there appears to be no selective absorbent for carbon monoxide, the problem is to find a catalyst by which the carbon monoxide will be oxidized in the presence of hydrogen. The solution of this problem has occasioned much research on the larger problem of the oxidation of carbon monoxide in general and under the influence of various catalysts. With this research are connected especially the names of J. C. W. Frazer and W. A. Patrick, W. C. Bray, A. F. Berton, and A. B. Lamb. While the subject of the fixation of nitrogen belongs to industrial research, the work of C. S. Bradley and F. W. Lovejoy ought to be mentioned as pioneer work, as well as the researches of J. E. Bucher, and the more recent work of E. W. Guernsey and M. S. Sherman on the fixation of nitrogen as sodium cyanide, in which they have studied the equilibria involved in the successive formation, from Na_2CO_3, Na_2O, Na, Na_2C_2, to NaCN. Nor should, for the sake of old times, a paper by A. A. Breneman be overlooked, which was published in an early issue of THE JOURNAL, giving a review of the subject of fixation of nitrogen as it then appeared, a valuable paper for its time, and possibly foreshadowing some of the more recent work.

The Platinum Metals

Looking back once more to the latter portion of the last century, we find in W. L. Dudley one who did much work in inorganic chemistry, little of which found its way into print. He was particularly interested in the platinum metals (from his association with John Holland, in whose laboratory he for a time was employed), and devised a method for melting iridium by adding a small amount of phosphorus. This alloy of iridium with iridium phosphide was brittle and could be broken up, and much of the phosphorus roasted out. These fragments found an important use in tipping gold pen points in place of the natural iridosmium flakes. This reminds us of Achard's process of fusing platinum by adding arsenic, and it was this first method of getting malleable platinum that may have suggested to Dudley the idea of using phosphorus with iridium. Dudley also found that platinum could be dissolved in hydrochloric acid if air is present, a method later developed for the preparation of chloroplatinic acid by the use of hydrogen peroxide as an oxidizing agent, thereby avoiding the nitro compound formed when nitric acid is used. Dudley's most important work was his study of the action of sodium peroxide on metals, especially on those of the platinum group, most of which are attacked by this reagent. Dudley was also one of those who was interested in the anomalous position of tellurium in the periodic table, and published a paper reviewing what had been done to resolve the difficulty. It was the ordinarily received view that tellurium was really a mixture with a homolog of higher atomic weight, and many were the efforts to separate the supposed mixture into its constituents. Dudley examined specimens variously fractioned with the spectroscope but found no evidence of complexity. W. R. Flint had at first effected a seeming separation by hydrolysis of the chloride, but J. F. Norris and Henry Fay, by fractionation of potassium bromotellurate, failed to find any sign of complexity. The work of W. C. Morgan, also on the hydrolysis of the chloride, seemed to settle the question in favor of ordinary tellurium being a simple element, and this view obtains today. The anomalous results of Flint, and of Flint and P. E. Browning remain to be explained. Browning has greatly extended our knowledge of many of the rarer elements, and his work should be mentioned here, though much of it has been with a view to analytical separations. The work of J. F. Norris on the isomorphism of selenium and tellurium should be noted in connection with the place of tellurium in the periodic table.

Reaction Products of Phosphorus Oxychloride

An important research in the last decade of the last century was that of H. N. Stokes on the reaction products of phosphorus oxychloride, $POCl_3$. His first work was with the silicic acid esters, which led to the production of a chloride of silico-pyrophosphoric acid. This was followed by papers on the reaction of phosphorus oxychloride with ammonia, which led to very interesting results, this reaction giving several series of amino and imino phosphoric acids. While Stokes made for the time a very full investigation of the subject, he left much that might be done, and pointed the way to the possibilities of similar amino and imino compounds with other less familiar acids. Of course this work ties on to Franklin's ammono compounds, but represents mixed ammono and hydro compounds.

Sulfur Problems

A number of problems connected with sulfur have been studied by American chemists in this half-century, an early research being that of L. W. McKay on the reaction between hydrogen sulfide and arsenic acid. It had been handed down from early literature that the action of hydrogen sulfide was to reduce the arsenic to arsenious acid, and that only arsenious sulfide and free sulfur are precipitated. McKay showed that here, as in so many other cases, everything depends on the conditions, and that it is quite possible to precipitate the pentasulfide. He also discovered the trithioarsenic acid, which is involved in the reaction. This work was all later confirmed in the light of modern methods by William Foster.

The problem of the preparation and composition of the hydrogen polysulfides is an old one, and many chemists have worked on it with various results. Quite recently J. H. Walton has again attacked the problem and from the oily liquid obtained by running a solution of the sodium polysulfides into cold hydrochloric acid, which produces a mixture of the polysulfides of hydrogen, he has isolated the disulfide and trisulfide, H_2S_2 and H_2S_3, in a state of great purity. These persulfides dissolve sulfur very readily and evidence was obtained of the existence of the hexasulfide, H_2S_6, which begins to decompose a little below zero.

The action of sulfur on alkalies has also furnished a perennial problem, which has in recent years become a very practical one, owing to the extensive use of the lime-sulfur wash as a fungicide, and the chemists of several government experiment stations have busied themselves with it. Much of this wash is purchased by farmers and much is homemade, and in both cases rule-of-thumb methods have been largely used in its manufacture. Hence the importance of the investigation of a very intricate reaction, very variable under varying conditions. H. V. Tartar finds that with hot caustic potash, K_2S_3 is formed, together with $K_2S_2O_3$, and with more sulfur, K_2S_5, while with lime and sulfur, CaS_4 is formed, also taking on more sulfur to form the pentasulfide.

With metallic sodium and excess of sulfur in boiling toluene the trisulfide is formed, while under like conditions with metallic potassium the product is the pentasulfide. It would not be venturesome to predict that the last word on the action of sulfur on alkalies has not been said. With the introduction of lead arsenate as an insecticide, and later of calcium arsenate, it was necessary to work over old material in the light of newer chemistry, and C. C. McDonnell and H. V. Tartar have pretty well cleared up the lead arsenates; C. M. Smith has done the same for the lime-arsenic acid equilibrium, while Story and Anderson have studied the arsenites. The work of these chemists has revealed how much there is yet to be learned of the chemistry of old and familiar things.

Radiochemistry

So much of the field of radiochemistry is really inorganic that at least allusion must be made to the work of B. B. Boltwood and of S. C. Lind on radium, Boltwood's discovery of ionium, and Lind's work on the chemical reactions produced by the alpha particle. Similarly, Irving Langmuir's work on chemical reactions at infinitesimally low pressures belongs in another field and must be passed over with a mere mention.

Recent Miscellaneous Investigations

So, too, must be omitted numerous other pieces of work which it would be worth while to dwell on did the limitations of this chapter permit. Such are, for instance, the work of W. F. Hillebrand on the isomorphism of thorium and uranium; of Edward Hart on glucinum; of T. W. Richards and of D. W. Horn on the cuprammonium compounds and of W. D. Harkins on the cobaltamines by physicochemical methods; of Allen Rogers on molybdenum and F. C. Mathers on indium; of A. B. Lamb on periodic acid and of Maxwell Adams on hydroxylamine; of E. E. Reid on perchromic acid and of H. H. Willard and of F. C. Mathers on the preparation of perchloric acid; of H. R. Carveth on the electrolytic deposition of chromium, now twenty years later being put into practical application, thus fulfiling his prediction that as the plated metal is very hard, it is capable of industrial use; of L. J. Curtman on double arsenates and phosphates; and of H. I. Schlesinger on the double fluorides of the platinum group; of E. G. Mahin and of William Blum on the constitution of the aluminates; and finally F. W. Bridgman's discovery of two new modifications of phosphorus and Leonard Hasche's discovery of a new oxide of nitrogen, N_3O_4.

Conclusion

As was stated at the opening of this chapter, conditions can hardly have been considered favorable for research in pure inorganic chemistry in America, and if it *is* pure inorganic chemistry it must today largely pass over into the realm of physical chemistry. On the other hand, using the methods of physical chemistry, the field of inorganic chemistry is enlarging at a rapid rate; we are realizing how every step taken in what was the large field of inorganic chemistry a century ago is today merely a starting point for new research. On still another hand, the applications of chemistry to industry are increasing by leaps and bounds, in both inorganic and organic realms, and problems of volume production and efficiency are largely depending on the physicochemical study of inorganic and organic compounds and reactions; general chemistry it all is.

CHAPTER IX

ORGANIC CHEMISTRY

BY TREAT B. JOHNSON

Introduction

The historians, who write of human evolution, speak of the Stone Age, the Bronze Age, the Iron Age, and other Ages, meaning by such distinctions the successive periods of human activity that have been characterized by the use of these materials. A quite fitting term to apply to the period in which we are now living, and which began about one hundred years before the birth of our national SOCIETY, would be "The Chemical Age." It has been one of rapid and wonderful developments. Many pages could be written to illustrate how far-reaching and how marvelous have been the modern advances in chemical science and their applications. But all this has taken place so quietly that the average individual does not appreciate the part these new discoveries are playing; nor can we estimate with any accuracy the still greater part they are to play in the future.

It is, therefore, a duty and a privilege for us, as chemists, to reveal at this time and in this fitting place a picture of our major accomplishments and their meaning, which will be understandable to those who have not had the opportunity to study chemistry. It is next to impossible today for the layman to form any proper appreciation of how far the results of chemical science are of influence in his daily life, still more to what an extent they are likely to come to his assistance in the future. In our relations with our fellow men, and when we are rejoicing as scientists over the results of our past accomplishments, let us not forget that it is only recently that the progress of pure scientific knowledge has caught up with the old empirical methods of the industrial operations of our manufacturing organizations. Organic chemistry in America is a very young science.

The task of reviewing the progress of organic chemistry in our country since the organization of our national SOCIETY in 1876 is not an easy one. The growth has been so rapid and so many outstanding achievements in the pure and applied fields of this branch of chemistry have been accomplished, that it is an impossibility, in an essay of this size, to evaluate the work of every investigator who has played an important role in this development. Although I have not suffered myself to overlook any facts and accomplishments that were known to me or were brought to my attention, I have, however, realized my limitations as an historian of organic chemistry. In bar of any criticism that may be brought against my survey and conclusions, I can only offer the same apology for human frailty as was expressed by Benjamin Silliman of Yale in his address on "American Contributions to Chemistry," delivered at Northumberland, Pennsylvania, August 1, 1874, on the occasion of the Priestley centennial of chemistry. I quote his words verbatim:

> In attempting to review the contributions to our science at the hands of American investigators during the century we celebrate today, it is proper in bar of criticism to say that I was called at a very late hour to the task in hand, and have become more sensible as the work opened before me of the disproportion between the brief time at command and the extent of the task assigned me. If important omissions are detected—and that there are such can hardly be doubted—the speaker must beg of his fellow workers in the common field some indulgence, as is due to human frailty; and while he is conscious of a desire to do full justice to the labors of all, he has also the knowledge that all among living laborers have not responded to his call for coöperation. If an apparently undue proportion of space has been given to some portions of the historical part of our essay, it may be said in fairness that it is far easier and more just to write history than to anticipate it, and one who lives in this latter end of the first century of modern chemistry must see to it that we leave such footprints in the sands of our time that the future historian of the science cannot fail to do us justice.

The Growth of Organic Chemistry as a Science

There is probably no topic which is better suited than organic chemistry to indicate the advance which has been made in this country, since the organization of our national SOCIETY, in teaching, research, and the various lines of active work of our science. In 1876 the science of organic chemistry was, indeed, very highly developed in Europe and there were many productive workers in Germany, France, England, and Russia, whose achievements preceding this date are now recognized as foundation stones of our present scientific structure. But at that time in our own country there were only five or six universities in which organic chemistry was taught as a special branch of chemistry, and in which researches in this special field were conducted. Those who were interested in the promotion of the science were unable to accomplish their aims on account of lack of funds and laboratory equipment.

Alexander Smith
(1865–1922)
President 1911

Foster

Arthur D. Little
(1863–)
President 1912, 1913

Theodore W. Richards
(1868–)
President 1914

Gessford.

Charles H. Herty
(1867–)
President 1915, 1916

C. H. Herty was also Editor of *Industrial and Engineering Chemistry* 1916–1922.

In the early period of organic chemistry formula worship was a strong force influencing the researches in this subject, and the remark is made even today, by those who have not followed the modern developments, that on account of this worship the evolution of organic chemistry has been retarded and conspicuous progress is not being made. We have also been subjected to the criticism that our native publications do not stand out as constructive and original contributions to our science. The author does not believe that this is a just and warranted criticism, and he feels quite confident that there is an increasing discontent among our young investigators with the simple development of ideas inherited from the past. We have growing in our country a most promising group of young chemists, who can be expected to add to the present knowledge of our science.

The constitution or structure of chemical compounds has received more attention from organic chemists than any other subject, and this has been true ever since chemistry came to be a science. Just as soon as organic chemists recognized the significance of structural or space formulations of organic molecules, the science began to undergo a rapid evolution and an advance was made which has never been duplicated. It was the physiologist and philosopher, Du Bois-Reymond, who said:

> I know of no more astonishing production of the human mind than structural chemistry. To develop, from that which appears to the five senses as quality and transformation of matter, such a doctrine as that of the relations between the hydrocarbons, could scarcely have been easier than to develop the mechanics of the planetary system from the motion of luminous points; and Strecker's prediction of the synthesis of creatine, which was afterwards verified by Volhard, although in a less exalted sphere, was in fact no smaller achievement than the discovery of Neptune.

What a wonderful advance has been made since Du Bois-Reymond spoke these words! Organic chemists have not been pursuing a phantom for the past fifty years. The success attending the application of the doctrine of valency to the compounds of carbon helped its extension to all compounds formed by combinations with this element. Edward Frankland and August Kekulé gave us great truths. No conceptions more prolific of results have been introduced into any department of science, and this very success in the hands of the organic chemists is now making it more and more obvious that these are truths which are worth pursuing for further development from the physical side. Valency was the ladder by which the organic chemist climbed to his brilliant achievements in chemical synthesis; but notwithstanding this success, there is something to be reckoned with besides valency. One great desideratum of modern organic chemistry is a physical interpretation of the combining capacities of the carbon atom.

Many organic chemists today are unwilling to admit, as many would have them to believe, that the chemistry of carbon has reached its limit of development. There is a growing spirit of optimism among a large proportion of our young workers that organic chemistry has not approached that condition in which it has ceased to afford a profitable field for research. The writer is one who believes that never, since the organization of our SOCIETY in 1876, has there been a time when there were more opportunities for constructive and original work than are visible at the present time.

From the systematic point of view there is no doubt that organic chemistry is the most highly developed branch of chemistry. The old idea that the only aim and end of organic chemistry is that of making new compounds, and then studying their constitution, is not the doctrine that is practiced by organic teachers in our most progressive institutions. Every science naturally develops along the line of least resistance, and in the case of organic chemistry this was synthesis. In the early sixties scarcely an organic chemist concerned himself with the relative positions of atoms or groups of atoms in space, and it was nearly twelve years after the birth of our SOCIETY that organic chemists awoke to the importance of this special relationship. In other words, while Pasteur's conception of molecular asymmetry was enunciated in 1860, it was not until 1874, when the classic papers of van't Hoff and LeBel appeared, that Pasteur's ideas assumed a development applicable to the theory of structures; and not until 1887 that Wislicenus showed that stereochemistry is no longer a chemical curiosity. The introduction of the stereochemical hypothesis was unquestionably the greatest advance in structural organic chemistry since the recognition of the quadrivalency of carbon.

Following this work of Wislicenus this subject became a fashion, has remained so ever since, and it is gratifying to write that the influence of his work spread to America (the home for a time of his youth and the scene of his early chemical labors), and that some of the most important contributions in this field today are being made by American organic chemists. We are now concerned, as never before, with explanations of physical structure, and in no field of science are these speculations to find a greater field of service than in that dealing with the problems of physiological chemistry.

The organic chemist of the last fifty years has been more than a mere interpreter of nature. A marvelous perseverance and constructive ability has been displayed. He has developed powers of synthesis beyond those of nature. Although the early aim was directed to the discovery of the arrangement of atoms within molecules, more and more attention is now devoted to the way in which the specific reaction takes place. Physiological chemistry has been revolutionized by application of new principles, and has now become a science of progress. Bacteriology is also being influenced by the same forces. The organic chemist hitherto interested himself chiefly in the end products of his reaction. By appropriating the principles of physical chemistry in his work, he has come to realize that his reactions do not proceed to end in a sense expressed by his graphical equations, but that reaction velocity and laws of equilibrium exercise a fundamental bearing on his whole work. He has learned to realize that his equation is true only when read from left to right and vice versa from right to left.

It can be truly said that the trend of organic chemistry is gradually away from a narrow conception of structural formulas as the final goal, and towards a consideration of nature as a manipulation of energy. The continuity of all classes of chemical phenomena is being more and more recognized, and as a result we are seeing the evolution of a new kind of chemistry—biochemistry. This is attracting the attention of some of our best workers in the fields of organic and physical chemistry. In no country is more progress being made today in this new field of chemical science than in America. Several of our leading American workers in organic and physical chemistry are engaged in its development and through the results of their investigations they are contributing very extensively to the advancement of medicine, physiology, and bacteriology. No one of these branches of science can advance further without the aid of chemistry. The human body is now recognized as a chemical laboratory, and without the aid of the chemists qualified with a thorough knowledge of the properties of carbon its mysteries cannot be unraveled. We are at the beginning of a new era and great advances are to be expected.

The present status of biochemistry is well expressed in the words of Meldola, who wrote in 1895 as follows:[1]

> We are but dwellers in the outer gates, waiting for the guide who is to show us the bearing of modern research on the great problem of life, which confronts alike the physicist, the chemist, and the biologist.

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[1] *Nature*, **52**, 482 (1895).

It was E. F. Armstrong who wrote in 1924:

> Chemistry, in particular organic chemistry, is perhaps today at the parting of the ways, and we may well be on the eve of another great advance due to the birth of new views of structure. Earnest workers in all branches of the science are making strenuous efforts to see behind the curtain and are converging to a common view—a sure sign that a renaissance is at hand.

The Period 1876–1901

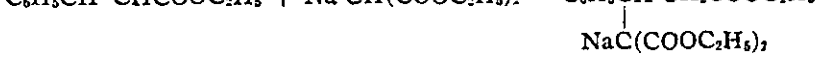
The writer has necessarily confined himself to the field of academic activities, and left for other writers to review the developments which have been made in the field of applied organic chemistry and to relate the history of the marvelous growth of our modern organic chemical industry. Scientists and technologists in organic chemistry are not born, but made by half a lifetime of hard study, and in both fields we can point to several outstanding men in this country whose achievements in special lines of research have been the directing influence leading to great scientific and industrial accomplishments. Research men and teachers in academic institutions have a way of giving more than they receive, and in their collegiate activities they have many opportunities of being kind and helpful. Very often, however, little reward is offered for such assistance, and in many cases the information given has contributed to the success of important commercial developments. In some cases it is often impossible for industry to repay these men or even to show a due appreciation of their services. We have had many examples of men of this type in the field of organic chemistry in our country, and their influence has been of the very highest value to the progress of our science.

When one attempts to present a picture of the progress made in the field of organic chemistry, and to discuss the present status of this branch of chemistry he is at once confronted with the question, which naturally arises in the minds of anyone who is interested, as to who have been the outstanding personages in bringing about this pronounced change in chemical interest in this country during the past fifty years. One is immediately asked, is it a growth of recent years and of the mushroom type, or were the foundation stones of our present structure laid several years ago in the early period of our development? In other words, can we pick outstanding figures who may be classified as a group of pioneers, or was our superstructure built on the results of researches of our present generation? It is perhaps fortunate for the writer that he is in a position to visualize and obtain a prospectus of the progress of our achievements from a central station. It was in 1901 that he received his Ph.D. degree from Yale University, or the same year that our SOCIETY celebrated its Twenty-fifth Anniversary. In consequence of this fact he is led to draw illustrations and comparisons from these two definite periods of our history and to emphasize the outstanding academic achievements of the two periods, 1876–1901 and 1901–1926. To answer the above question is extremely difficult. Only those chemists can be mentioned who stand out in bold relief. Some of our most brilliant researchers in science started their careers as workers in organic chemistry, but did not stay in this field. They shone later by the results of their outstanding performances in departments of knowledge other than chemistry.

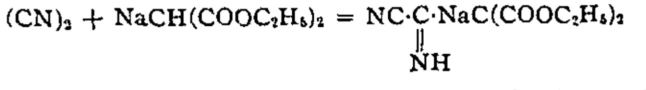
After a careful study and consideration of certain facts, which will be referred to later, the author is led to the conclusion that the progress, of which we are all proud, has been one of evolution and that the results obtained have been accomplished successfully by the application of sound and accurate principles which were taught to us by the men active in our old institutions of learning. In other words, as is well expressed in the words of one of our esteemed pioneers—Remsen—"Progress in chemistry is not made by revolution but by evolution." Space forbids an exposition of more than a mere reference to the most outstanding achievements. The final conclusion that any reviewer can safely draw, no matter what feature is emphasized, is that American research in organic chemistry is not the product of a selected group of geniuses who have shone conspicuously, and have, thereby, won a commanding position through notable achievements, but is the result of the labors of a large number of men working, for the most part, under very unfavorable conditions and against a pressure calling for the greatest personal enthusiasm. In other words, we are observing and enjoying the results of the mass action of a large group of interested workers.

There has never been any royal road in chemical research in organic chemistry. Each step in advance has always been made more or less at random, and each investigator is comparable to a traveler in an unknown country. His path is never mapped out for him, and there are many by-paths, which are always uncharted, leading him often in the wrong direction. There is only one course that is the right one to follow, and this has to be found by many trials. Our future advance and the new contributions to knowledge are dependent on our ability to benefit by the errors that have been recorded by our earlier explorers. In this light it is indeed fortunate that the men operating in the period covered by the years 1901–1926 can well turn to the labors of their scientific brethren who were active during the first period, 1876–1901, for inspiration and advice.

It is questionable whether any American investigator in the field of organic chemistry has contributed more of a fundamental character and has been more widely recognized outside of the United States for the originality of his theoretical concepts and conclusions than Arthur Michael. His defense of the Kekulé-polymolecule idea, and his interpretation of the mechanism of an organic reaction as proceeding according to the principles of addition, with formation of an intermediate "addition product," were conceptions which have exercised a tremendous influence on the development of chemical thought. He can justly claim first place among American chemists during the last fifty years as an exponent of original chemical theory, and any survey of our fifty years of progress would not be accurate if it did not reveal the accomplishments of his researches and refer to the influence that his work has had on the development of chemical thought since the beginning of his activities as an organic chemist. He has formulated principles, made and originated syntheses and discoveries leading to applications which have rendered the world a service much greater than is generally known. Michael has not only influenced modern chemical thought on the subject of mechanism of chemical reactions, but he has also made most important contributions of theoretical bearing dealing with such subjects as valency, the relation of thermochemistry to organic structure, desmotropism, stereoisomerism, the theory of partition principle, and the scale of combined influence. In the field of organic syntheses may be recorded as outstanding accomplishments his original method of building up carbon combinations by the direct addition of malonic esters, in the form of their sodium salts, to unsaturated carbon compounds, as is illustrated by the two following syntheses:



$$C_6H_5CH\ CHCOOC_2H_5 + Na{\cdot}CH(COOC_2H_5)_2 = \underset{\displaystyle NaC(COOC_2H_5)_2}{C_6H_5\overset{}{C}H}{\cdot}CH_2COOC_2H_5$$



$$(CN)_2 + NaCH(COOC_2H_5)_2 = NC{\cdot}\underset{\displaystyle \| \atop NH}{C}{\cdot}NaC(COOC_2H_5)_2$$

It was Michael who first showed that urea and thiourea interact with malonic ester, in the presence of sodium ethylate as a catalyst or condensing agent, to form cyclic ureides or pyrimidine condensations, and in his work on the production of salicin from synthetical helicin he won the distinction of being the first one to accomplish successfully the synthesis of a glucoside occurring in nature.

The second American investigator who was conspicuous for his advanced views regarding the mechanism of organic reactions, and whose original conceptions attacked the very foundation of the theories regarding organic reactions, current at the time he was active, was John Ulric Nef. His denial of two fundamental assumptions, namely, that of the constant quadrivalence of carbon in organic combinations and that of the assumption of molecular substitution as representing the primary mechanism of many of our organic reactions, was considered revolutionary by many of our organic investigators; yet it cannot be denied, in the light of modern developments, that his speculations have contributed to some of our most important and fundamental work. His researches and speculations on unsaturation of organic compounds, the structure of nitro paraffins, the nature of valency, the bivalency of carbon, the structure of mercury fulminate, intramolecular addition-reactions, methylene carbon chemistry, and the theory of addition-reactions have been achievements of outstanding merit and importance. So important was bivalent carbon according to Nef that he expressed the conviction in one of his papers, "That in the chemistry of methylene is to be found exact scientific physiology and medicine and perhaps an explanation of the vital processes."

It is undoubtedly true that these two men—Michael and Nef—are the outstanding figures of the older school in the field of theoretical organic chemistry in this country. Unfortunately, their work is not so well known to our present American investigators as it should be, as most of their papers were published in German journals. Too few of us realize how much several of the German journals owe to American contributors of our first quarter-century, 1876–1901, for their past success. The two most interesting and important conceptions which have enriched organic chemistry within the last fifty years were formulated by these two American organic chemists—Michael and Nef—but their ideas were developed in German publications. Germany was the leader of the chemical world at the time they were most active, and naturally their papers were sent to those journals where they were assured prompt publication and were read by chemists in Europe who were recognized as leaders in their profession.

Neither of these two men will be remembered for his influence as a great teacher. They were, on the other hand, representative

Julius Stieglitz
(1867–)
President 1917

William H. Nichols
(1852–)
President 1918, 1919

Harris & Ewing

William A. Noyes
(1857–)
President 1920

Edward C. Franklin
(1862–)
President 1923

W. H. Nichols was also a Charter Member; W. A. Noyes was also Secretary 1903–1907, Editor of *Journal of the American Chemical Society* 1902–1917, and Editor of *Chemical Abstracts* 1907–1909.

of a very small group of men, active in the first decade of our period of history, who were gifted with an unusual natural ability for original research and fortunately enjoyed opportunities for cultivating it. While one (Michael) excelled as a theorist and as a keen critic in the field of organic chemistry, the other (Nef), though often criticized for not presenting sound theory, excelled as an experimentalist of the first rank and supported his own speculations with original data.

Men of a different stamp, who were active in our first period, and who cannot be forgotten in this review were: Josiah P. Cooke (1827–1894), an educational pioneer who took a very prominent part in the contest of introducing science into our college courses and advocated strongly the laboratory method of teaching chemistry; T. Sterry Hunt, who was the first to define organic chemistry as the chemistry of carbon and was very active in the field of chemical speculation; and A. B. Prescott, who was made professor of organic chemistry at the University of Michigan in 1876. The latter's textbook on "Organic Analysis" was the most complete and valuable treatise on this subject that had yet been written by an American chemist.

Organic chemists in our country owe a debt of gratitude to Ira Remsen, not only for his achievements as an investigator in the field of organic chemistry and as an excellent teacher, but chiefly for his organization, support, and service as editor of the *American Chemical Journal* during its period of publication from 1879 to 1913. For his research work on saccharin the Society of Chemical Industry in England conferred upon him the medal of that Society and thus recognized for the first time in its history the discoveries of an American chemist.

The *American Chemical Journal* offered a medium for publication of original research which was greatly needed in this country. It acted as an important stimulus to American research in both organic and inorganic chemistry and received the support of the best workers in our American universities. It was one of the chief factors which served to develop or create a national interest in the contributions of American investigators; it stimulated a competition which led to a decided increase in the amount of published work in this country, and discouraged the habit of foreign investigators of ignoring and belittling American chemistry. At the time that the journal was started practically all the results of the best research work done in this country were published abroad. Today the tables have been reversed, and the fact that a condition has been developed whereby only an occasional American investigator publishes in a foreign journal is due in no small degree to the vision, love of American institutions, and scientific interest of Ira Remsen. He has ever been a strong supporter of original research, and his pleas for a more thorough study in our country of modern organic chemistry have always been received with enthusiasm and met with prompt support.

The *American Chemical Journal*, while edited with the aid of chemists in America and abroad, was supported chiefly by workers in this country. Its pages record the results obtained by the most active organic researchers of that period. Some of the prominent organic chemists who contributed extensively to the support of that journal during its thirty-five years of activity, in addition to Remsen and his co-workers, were the following:

W. G. Mixter	Sheffield Scientific School of Yale University
S. P. Sadtler	Philadelphia College of Pharmacy
S. W. Johnson	Sheffield Scientific School of Yale University
C. L. Jackson	Harvard University
E. F. Smith	University of Pennsylvania
F. W. Clarke	University of Cincinnati
Arthur Michael	Tufts College
J. M. Crafts	Geneva, Switzerland, and Amherst College
E. J. Hallock	Columbia College
H. B. Hill	Harvard University
W. J. Comstock	Sheffield Scientific School of Yale University
J. U. Nef	Clarke University and University of Chicago
Felix Lengfeld	University of Chicago
Paul C. Freer	University of Michigan
T. B. Osborne	Connecticut Agricultural Experiment Station
R. H. Chittenden	Sheffield Scientific School of Yale University
H. L. Wheeler	Sheffield Scientific School of Yale University
T. B. Johnson	Sheffield Scientific School of Yale University
Julius Stieglitz	University of Chicago
W. A. Noyes	University of Illinois
Moses Gomberg	University of Michigan
J. F. Norris	Massachusetts Institute of Technology
J. R. Bailey	University of Texas
E. P. Kohler	Harvard University
R. S. Curtis	University of Illinois
H. A. Torrey	Harvard University
H. D. Dakin	Laboratory of C A Herter, New York City
L. W. Jones	Princeton University
H. W. Wiley	Bureau of Chemistry
J. H Kastle	State College of Kentucky

Among the most outstanding contributions in organic chemistry made by these various investigators may be mentioned the following:

(*a*) The various papers by Remsen and his collaborators on the chemistry of sulfonic acids

(*b*) Publications by Arthur Michael on the synthesis of helicin and salicin, the constitution of ethyl acetoacetate, stereoisomerism, and the law of entropy.

(*c*) The development and application of the Friedel-Craft reaction, reported in Remsen's journal in 1879.

(*d*) Synthesis of saccharin by Remsen and Fahlberg.

(*e*) The discovery of furfural as a product of the dry distillation of wood by Hill in 1881, and later contributions to the chemistry of mucobromic acid.

(*f*) Chittenden's pioneer work in the field of physiological chemistry, including yearly reviews of the progress of this branch of chemistry.

(*g*) Paper on sodium formanilide by W. J. Comstock and F. Kleeberg. This is of particular interest as the first case of a compound containing the —NHCO— grouping, whose sodium salts, under conditions which exclude dissociation, interact with alkyl halides to give nitrogen ethers, whereas the corresponding silver salts give the oxygen ethers.

(*h*) Crystalline vegetable proteins by T. B. Osborne and co-workers.

(*i*) Contributions to the chemistry of camphor and camphoric acid by W. A. Noyes.

(*j*) Molecular rearrangements and the chemistry of pyrimidines. Synthesis of the natural biochemical combinations—uracil, thymine, and cytosine—by H. L. Wheeler and T. B. Johnson.

(*k*) Salts of imido esters, theory of the Beckmann rearrangement, and studies in catalysis by Stieglitz.

(*l*) The discovery of triphenylmethyl by Gomberg. Trivalent carbon.

(*m*) New applications of the Grignard reaction, and contributions to the problem of unsaturation by Kohler.

(*n*) Application of the principle of β-oxidation and its biochemical significance by H. D. Dakin.

It was G. C. Caldwell in his address on "The American Chemist: His Past and Present" who stated in 1891 as retiring President of the AMERICAN CHEMICAL SOCIETY that:

> The most frequent contributors were Clarke, Chittenden, Gibbs, Hill, Jackson, Morse, Michael, Mabery, Mallet, Remsen, Smith, and Wiley. The most notable feature in the work of this decade is the great amount of work in organic chemistry done especially under the leadership of Remsen, Jackson, and Michael, most of which found its way to the public through Remsen's journal.

It was due to the self-sacrifice of these various men, who supported the *American Chemical Journal* in the early and dark days of American chemistry and who forced their papers into that journal for publication, that a condition was finally brought about compelling foreign recognition of our work. A notable feature in the work of this first period was the great amount of research done in organic chemistry, and we can all feel confident and proud that it was not work of which an American need be ashamed. We can all rejoice as organic chemists that our own country contributed in those early days in so large a measure to worthy research.

In completing this review of the first period of our history—1876–1901—the writer can conclude the chapter with no finer remarks than those of that great historian of chemistry—Schorlemmer—who translated the preface to Hermann Kopp's "Die Entwickelung der Chemie in der Neueren Zeit" as follows:

> To none is it allowed to enjoy for long the progress of science, and the results which the future may bring to light. The alchemists of past centuries endeavored to prepare the elixir of life, a means by which man might be kept

healthy in body and mind for an unlimited space of time. We will not discuss here the question how far this might have been an advantage for science if eminent men would have continued their researches for an unlimited period. The alchemists worked in vain. It is not in our power to appropriate to ourselves the experiences and the results which futurity alone can bring. But in a certain sense we are indeed enabled to prolong our life backward into the past by appropriating the experiences of those who were before us, and by becoming acquainted with their views as thoroughly as if we had been their contemporaries. The means of doing this is also an elixir of life. May the present attempt to contribute to this end be judged with indulgence.

The Period 1901–1926

As early as 1890, the opinion was expressed in England and on the continent by chemists who sensed the trend of developments in chemistry, that the greatest advance in future years would take place in America. Although European countries stood in the forefront at that time, it was felt that conditions were such in America that we were destined to take the lead in a not distant date in both industrial and scientific achievements. This prophecy has to a large extent been fulfilled, and the success of our achievements is due in no small degree to the research activities carried on by our organic chemists during the last twenty-five years. If one takes this second period of our history, 1901–1926, and attempts to award to it its full measure of distinction, it is very questionable whether any previous period of twenty-five years has contributed so much, in all fields of pure and applied science, that has affected so materially the progress of the whole world, and has benefited the general welfare of every human being. As a result, the status of the profession of chemistry has been raised to a much higher level, and the public now appraises our professional services with a far greater appreciation than formerly. Organic chemists in America who are qualified for advanced research enjoy the satisfaction of feeling that there is a market for their services. This condition did not prevail in 1901, as the writer can well attest from experience. We now enjoy a rare advantage, and we feel grateful for the part our national SOCIETY has played as an organization in developing and perfecting the present condition.

The progress of organic chemistry during the past twenty-five years has been helped by the recent developments in the field of physical chemistry. The new advances made in this branch of chemistry have been an assistance, and have in no way interfered with the major study of the constitutional problems under investigation by the organic chemists. In fact, the new revelations of crystal structure by application of the principles of X-ray analysis have led to results which have confirmed the older speculations regarding the structure of organic compounds. The newer discoveries have made it possible for the organic chemist to give interpretations to many phenomena which are an improvement over those given by our earlier workers. This has in no way led, however, to a revolution of the methods of organic chemistry. While the new tools presented for our use by the physical chemists have enabled us to make greater progress in our own special field, we are still unwilling to admit that the fruitful conceptions of Kekulé do not still hold much in store for us. Neither are organic chemists inclined to take an extreme view as a result of the new advance made in our knowledge of the atom. They still believe in the atomic theory, which has proved so useful a tool in their past achievements, and that the organic chemistry of the future will be built upon the old. In other words, a greater science of organic chemistry will be developed in the next quarter-century period if we do not forget the achievements of 1876–1901 and also those of 1901–1926. The development will not be brought about by revolution, but by evolution.

Organic chemists are still confined to conditions widely removed from those which find application in the fields of the mathematical sciences. This branch of chemistry is probably still the most wonderfully elaborated section of chemical science, and like the biological sciences it must be developed for a long time on a non-mathematical basis. We have still much to accomplish by the empirical method. The organic chemist has a great deal to learn regarding the mechanism of organic reactions, and the present methods of experimental science compel the investigator to adopt a special technic and work with quantities which fail to reveal any variations in mass. Furthermore, the synthetical chemist is conscious of the possible creation of thousands of new organic combinations which theoretically may be predicted to exist. These new constructions when synthesized will open up still greater and richer fields for future research. It is, therefore, for such reasons as these that the organic chemist considers the basis of our present atomic theory a safe and secure foundation for future guidance in his investigations and speculations.

The major problem before the organic chemist is still that of acquiring a more exact knowledge of the organic molecule. What we need is a better knowledge of the methods of divining it, and to learn more regarding the energy relations and stray forces which operate to regulate and control the chemical activity of such organic complexes. Any method of attack which will enable the organic researcher to make a new advance should be appropriated. It is not a question of deciding at this time what method of attack will prove the most profitable, but one of utilizing all the methods which can be placed at our command. It was Professor Nernst who wrote:

> The question whether chemistry has profited most by the atomic theory or by thermodynamics is a foolish one. It is like the question whether Goethe or Schiller is the greater poet. Let us rejoice that we have two such valuable methods of chemical research. We need all the aid we can possibly get and even with this aid progress will be relatively slow.

A characteristic feature of the development in organic chemistry during the last twenty-five years has been the tendency to specialization. Fifty years ago the term "chemist" indicated a scientist with an encyclopedical mind, or one who was versed in all branches of chemistry—analytical, organic, and general or physical. Today it is impossible, on account of the rapid increase in scientific data, for a man to be master of any one single branch of chemical science. Organic chemistry has found such wide application to the solution of problems in other branches of science and in industry, and has proved of such great assistance in the solution of border-line problems in fields related to chemistry, that it has acquired a greatly extended field of utility and service. It is necessary today for one to limit his research activities to a special section of organic chemistry. As a result of this intensive specialization, a condition has been created which sharply differentiates our second period from the first. In the first, 1876–1901, it was possible to pick out certain workers who were outstanding personages in the whole field of organic chemistry. In this second period, which is now drawing to a close, it is much more difficult to decide "Who's Who in Organic Chemistry," and in consequence of the large number of men who have made noteworthy contributions in some special field, the author is forced to refer to groups of workers and their achievements, rather than to emphasize the accomplishments of any individual worker. In other words, we have made progress during the past twenty-five years as a result of mass action, and it is undoubtedly true that this condition has resulted in increasing the number of promising workers in our science.

The Division of Organic Chemistry of the AMERICAN CHEMICAL SOCIETY has a membership of nearly six hundred chemists, of whom not less than twenty-five have acquired a national reputation through their research accomplishments. Of the various chemists who have been honored in this country by election to the National Academy of Sciences for outstanding accomplishments in some branch of organic chemistry, sixteen are living. Of these, all but three—C. L. Jackson, Arthur Michael, and Ira Remsen—are still active and are contributing to our knowledge of this science, or to the development of border-line problems in the field of biochemistry. The fact that this Academy has elected so large a number of our division of chemistry to membership is conclusive evidence of the progress of this particular field of science.

The development of the chemistry habit in our country during the last twenty-five years, and the astonishing popularity and interest in organic chemistry research is due in no small degree to the energy and activities of a group of workers who have given more than twenty-five years to the service of this science and who are now entering the third quarter-century period of our chemical history. The various universities and research institutions where these workers have given such loyal service are now recognized as the important centers of academic research in organic chemistry in this country and are attracting to their laboratories a large number of young research workers. A quarter of a century ago the American university that supported an outstanding organic investigator was an exception, and as late as 1901 the ability to carry on constructive organic research was not considered as a superior attainment.

A review of this character would not be complete without inclusion of some brief references to the work of the more prominent of this older group of organic chemists. The twelve men who stand out particularly for their accomplishments are:

Moses Gomberg, of the University of Michigan, who has enriched our knowledge of the chemistry of "free radicals" and opened up a new fundamental chapter in organic chemistry by his discovery of triphenylmethyl; J. J. Abel, of Johns Hopkins University, recognized for his original work on adrenaline and his recent contributions to the chemistry of internal secretions; William A. Noyes, of the University of Illlnois, recognized for his contribution to our knowledge of the chemistry of camphor, his later work on optical rotation, and his researches in connection with the problem of positive and negative valences; Julius Stieglitz, of the University of Chicago, who has contributed to our knowledge of the mechanism of molecular rearrangements, opened the way to a precise formulation of indicator sensitiveness, and was one of the first in this country to apply physicochemical methods to the solution of problems of organic chemistry; Marston T. Bogert, of Columbia University, known for his original work on quinazolines and his researches in the field of heterocyclic organic chemistry and synthetic perfumes; Elmer P. Kohler, of Harvard University, an investigator who has done fundamental work in theoretical organic chemistry dealing with the question of unsaturation and theory of addition-reactions and has added to our knowledge of the Grignard reaction; Treat B. Johnson, of Yale University, who has contributed to the development of the organic chemistry of nitrogen, added to our knowledge of pyrimidines and purines, and extended the application of organic chemistry to the field of biochemistry; E. C. Franklin, of Leland Stanford University, the recognized American pioneer in the development of the ammono system of organic chemistry; P. A. Levene, of the Rockefeller Institute of Medical Research, known for his important work dealing with the unraveling of the chemical structure of biologically important substances, and who, together with C. S. Hudson of the Bureau of Chemistry, has won recognition in this country and abroad for important discoveries in the field of stereoisomerism; T. B. Osborne, of the Connecticut Agricultural Experiment Station and Yale University, who is recognized as the father of protein chemistry in this country and has won international distinction for his work; and F. B. Power, of the Bureau of Chemistry in Washington, D. C., known widely for his original work in the field of plant chemistry.

Today we have as many institutions as we have states in our Union that can point to the accomplishments of promising investigators in organic chemistry. No university which does not command the services of good organic chemists and the resources of well-equipped laboratories can be regarded as secure. J. R. Bailey of the University of Texas, W. L. Evans of Ohio State University, G. B. Frankforter of the University of Minnesota, Lauder W. Jones of Princeton University, J. M. Nelson of Columbia University, W. Lee Lewis of Northwestern University, J. F. Norris of the Massachusetts Institute of Technology, J. A. Nieuwland of the University of Notre Dame, E. E. Reid of Johns Hopkins University, R. R. Renshaw of New York University, F. W. Upson of the University of Nebraska, A. S. Wheeler of the University of North Carolina, W. R. Orndorff of Cornell University, and W. M. Clark of the Hygienic Laboratory, United States Public Health Service, are conspicuous representatives of a group of organic chemists who have won recognition as efficient teachers and made contributions in research which have won approbation. We are just beginning to appreciate our opportunities and to make the most of them. Several of our younger men and most promising teachers are studying various problems of organic chemistry earnestly, thoughtfully, and carefully under the guidance of these leaders, and through their initiative we are bound to win a market for our science, develop new potential possibilities, and raise it to a much higher level.

It is to the younger generation in our universities that we must look in the future for discoveries in the field of organic chemistry of constructive value. We have now in the field several men of outstanding ability of whom may be mentioned: J. B. Conant of Harvard University, A. J. Hill of Yale University, F. C. Whitmore of Northwestern University, F. F. Blicke of the University of Michigan, Roger Adams of the University of Illinois, Morris Kharasch of the University of Maryland, Henry Gilman and R. M. Hixon of Iowa State College, Homer Adkins of the University of Wisconsin, C. E. Boord of Ohio State University, and H. A. Spoehr of California. A great many meritorious pieces of work have to be omitted. Most important contributions in organic chemistry have been made also by men outside of university laboratories, of which may be mentioned, for example, the work of H. D. Gibbs on the catalytic oxidation of naphthalene to phthalic anhydride, and that of J. M. Weiss and C. R. Downs, who successfully accomplished the synthesis of maleic acid from benzene by catalytic oxidation.

The subdivisions introduced below will serve to show the specialization which has developed in our last period as a result of the expansion of the field of organic chemistry. Other groups of workers might be arranged, but it is believed that the subdivision made embraces all the developments of major importance. In each group the names of those chemists who have contributed widely in their respective field are recorded; and younger men have been included who have recently published material of considerable merit. No attempt has been made to classify these workers according to merit, and in many cases a name has been incorporated in more than one group. In fact, there are several men who have been conspicuous for their contributions in widely different fields of organic chemistry. In the preparation of this list the author has included those chemists who have been active in applying organic chemistry to the solution of problems in biochemistry. This new development has been a characteristic feature of our productive work in recent years. The author realizes that some worthy worker in his respective field may have been omitted from this classification. Such omissions, however, are not intentional. A conscious endeavor has been made to reveal the fact that we have in this country a very strong and active group of productive workers in organic chemistry, and the list only serves to show who have been the most prominent as contributors to our journals. The various papers published in the *Journal of the American Chemical Society* and the *Journal of Biological Chemistry* have served as a basis of selection of the most representative men.

The author would not be expressing a proper appreciation of the work of his colleagues, if he did not call attention to two large groups of men who are playing as important a part in the promotion of organic chemistry as those men who have the ability and privilege of publishing new material. He refers particularly to that large group of men which is engaged in the important work of teaching organic chemistry, and to the second group which is employed in industrial organizations in this country. Both of these groups are necessary members of a "chemistry crew" of which the research man is the stroke oar. Just as long as these various workers operate in unison and pull together the chemistry shell will move to the front and American organic chemistry will make progress. Reference must also be made to the noteworthy accomplishments of a group of organic workers who have contributed to the literature in the form of organic textbooks, chemical monographs, etc. There are several publications of this character of which we, in this country, may well feel proud.

It is the belief of the writer that more attention will be paid to the publication of special scientific monographs in the next period of twenty-five years than in the one that is just closing. This will be a necessary result of intensive specialization in our science. The author sincerely hopes that this survey may be so received that the younger members of our profession who read it may catch some of the real spirit in which it has been constructed; something of that feeling which animates, stimulates, and encourages our leading investigators, and which is the final cause that leads to a vigorous growth in any science. Let no one think that organic chemistry in America is today founded on flimsy foundations and is not to make further progress.

Subdivisions and Respective Workers

(1) ORGANIC CHEMISTRY THEORY (VALENCY AND ELECTRON PROBLEMS): Moses Gomberg, Julius Stieglitz, W. A. Noyes, J B. Conant, K G Falk, H. S. Fry, J. M. Nelson, C. W. Porter, E. C. Franklin.

(2) ORGANIC SYNTHESIS
T. B. Johnson, M. T. Bogert, A. J. Hill, Roger Adams, H. T. Clarke,

R. R. Renshaw, Oliver Kamm, A. W. Dox, A. S. Wheeler, W. R. Orndorff, L. H. Cretcher, M. L. Crossley, G. B. Frankforter, W. J. Hale, J. B. Conant, Henry Gilman, F. C. Whitmore.

(3) Carbohydrates, Including Cellulose:
P. A. Levene, C. S. Hudson, E. J. Witzemann, R. M. Hixon, Harold Hibbert, W. L. Evans, W. L. Lewis, F. W. Upson, F. B. LaForge.

(4) Enzymes:
C. S. Hudson, H. C. Sherman, J. M. Nelson, J. H. Northrop, K. G. Falk.

(5) Hydrocarbons and Cycloparaffins:
Moses Gomberg, E. P. Kohler, J. F. Norris, B. T. Brooks.

(6) Heterocyclic Organic Chemistry (Including Purines and Pyrimidines):
M. T. Bogert, T. B. Johnson, J. R. Bailey, Dorothy Hahn, A. J. Hill, C. O. Johns, Oskar Baudisch, C. E. Boord.

(7) Proteins and Amino Acids:
T. B. Osborne, H. B. Vickery, H. D. Dakin, D. B. Jones, R. A. Gortner, T. B. Johnson, P. A. Levene.

(8) Molecular Rearrangements:
T. B. Johnson, C. G. Derick, Julius Stieglitz, L. W. Jones, L. O. Raiford, Arthur Lachman.

(9) Reaction Mechanism:
Arthur Michael, E. P. Kohler, Julius Stieglitz, J. B. Conant, Arthur Lachman, Harold Hibbert, F. F. Blicke, L. W. Jones, T B. Johnson.

(10) Fats, Cholesterol, Phytosterols, etc (Including Essential Oils):
R. J. Anderson, F. B. Power, Edward Kremers, E. K. Nelson, B. H. Nicolet, A. H. Gill, F. W. Heyl.

(11) Biochemical Synthesis (Chemistry of Animal and Plant Cells):
T. B. Johnson, H. D. Dakin, E C. Kendall, A. E. Osterberg, K. K. Koessler, M. T. Hanke, P. A. Levene, Walter A. Jacobs.

(12) Stereoisomerism:
P. A. Levene, C. S. Hudson, W. A. Noyes, Julius Stieglitz, J. W. E. Glattfeld.

(13) Sulfur Chemistry (Acyclic and Cyclic):
M. T. Bogert, E. E. Reid, F. B. Dains, D. E. Worrall, T. B. Johnson, C. E. Boord.

(14) Catalysis of Organic Reactions:
Roger Adams, C. E. Boord, Homer Adkins, H. D. Gibbs, C. R. Downs, J. M. Weiss, J. A. Nieuwland, J. B. Conant, Julius Stieglitz, J. H. James, Oskar Baudisch, W. D. Bancroft, H. A. Spoehr, H. A. Taylor.

(15) Metallo-Organic Chemistry (Arsenicals, Mercurials, Grignard Reaction, etc.):
F. C. Whitmore, W. G. O. Christiansen, W. A. Jacobs, Michael Heidelberger, C. S. Marvel, W. L Lewis, G. W. Raiziss, C. A. Kraus, Morris Kharasch, C. S. Palmer, E. P. Kohler, Henry Gilman, Marie Reimer, E. C. Franklin.

(16) Physico-Organic Chemistry:
J. B. Conant, J. F. Norris, C. G. Derick, C. E. Boord, Julius Stieglitz, E. J. Cohn.

(17) Alkaloids:
F. W. Heyl, J. O. Schlotterbeck, J. U. Lloyd, H. M. Gordin, H. C. Biddle, Walter A. Jacobs, Michael Heidelberger, J. F. Couch.

(18) Phytochemistry (Including Plant Products):
H. A. Spoehr, C. W. Porter, Oskar Baudisch, Edward Kremers, F. B. Power, R. J. Anderson, V. K. Chesnut, E. K. Nelson.

(19) Identification of Organic Compounds:
S. P. Mulliken, Oliver Kamm.

(20) Terpene Chemistry:
L. F. Hawley, W. A. Noyes, A. W. Schorger, Edward Kremers, Frank Rabak.

The Future

Outside of the applications of organic chemistry that have been made in our various industries, there are none which will exercise a greater economic influence and promotion of man's welfare and progress than the application of this branch of chemistry to medicine. Medical science has been advanced through distinct achievements in the field of synthetical chemistry. The resources of the chemist have been offered freely and the public has benefited by the discoveries made. While the physician is well qualified by education and by experience to give the public advice on matters of health and disease, how little does the public realize that the newer remedies he uses to improve sanitation, relieve pain, heal disease, and in preventive medicine are products originating or developed in the laboratory of the organic chemist! Surely the time is now at hand when the public must be given the true facts. The information should come from the highest sources of chemistry and be published over the names of men capable of presenting the facts and who are acknowledged as leaders in their profession.

IN CONCLUSION.—If the author were asked to prophesy the course of progress in the future development of organic chemistry, he could make no prediction more sound and probable than by quoting verbatim a recent statement from the pen of a former President of our national SOCIETY—William H. Nichols. The statement is taken from an address delivered by him in connection with the celebration of Prof. Edward Hart's fifty years of continuous service at Lafayette College on October 16, 1924, and is as follows:

> I will venture only one prediction. The most elaborate and delicate chemical works ever devised is the human body. Much has already been done by the chemist in delving into its secrets. Positive results have been obtained which have almost annihilated certain diseases and modified others. I predict that during the next half-century the chemist, working hand in hand with the physician, will discover the origin and nature of most of the enemies of the human body—notably that arch enemy, cancer—and not only alleviate their effects but absolutely prevent their sinister operations.

Underwood & Underwood

LEO H. BAEKELAND
(1863–   )
President 1924

Harris & Ewing

JAMES F. NORRIS
(1871–   )
President 1925, 1926

Alman & Co.

ALBERT C. HALE
(1845–1921)
Secretary 1889–1903

Harris & Ewing

CHARLES L. PARSONS
(1867–   )
Secretary 1907–

A. C. Hale attended the Priestley Centennial in 1874.

CHAPTER X

THE CHEMISTRY OF PHYSIOLOGY AND NUTRITION

BY GRAHAM LUSK

> In passing on to discuss the theme assigned to us, Medical Chemistry, we find ourselves entering upon a broad domain of investigation. We might enlarge upon the many and wide bearings of chemistry upon medical practice and show how indispensable it is to the best success of the practitioner; point out its grand achievements in the departments of physiology and pathology, and show how inseparable it is with the progress of medical science in all its departments—THEODORE GEORGE WORMLEY, 1876.[1]

The Development

Born a hundred years ago, Theodore G. Wormley (1826–1897) pronounced the words inscribed above, words which might have been written by one of us today. In 1877 Wormley succeeded Robert E. Rogers as professor of chemistry and toxicology in the medical department of the University of Pennsylvania. The year before this, in 1876, *John Marshall* (1855–) entered the medical school and shortly became assistant to Wormley. Marshall was lecturer, quiz master, as well as laboratory janitor in the service of his chief. In 1879 he studied at Göttingen with Wöhler, and later at Tübingen with Hüfner, and also at Christiania. He was closely associated with the medical department of the University of Pennsylvania throughout his life, becoming assistant professor of chemistry in 1889, and professor from 1897 until 1922. He taught the old-fashioned medical chemistry which he had learned from Wormley.

In 1903 he introduced *P. B. Hawk* (1874–), a pupil of Atwater and especially of Chittenden, into his laboratory. Hawk transferred Chittenden's course in physiological chemistry to Philadelphia, and therefore the Chittenden influence was responsible for the introduction of physiological chemistry in the modern sense into the University of Pennsylvania.

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[1] Address on "Medical Chemistry," Centennial International Medical Congress of Philadelphia

Until nearly the end of the last century chemistry was almost exclusively in the hands of the medical schools. Thus Marshall invited Theodore W. Richards, of Harvard, then a schoolboy at Germantown, to come to his laboratory on Saturdays and found the boy regularly sitting on his laboratory steps waiting for him on Saturday mornings.

R. Ogden Doremus (1824–1906) was a pupil and assistant of John W. Draper, of New York University, between 1843 and 1850. He was one of the founders of the New York University and Bellevue Hospital Medical College in New York City in 1861. He was a brilliant lecturer and an extraordinary teacher of undergraduates. He was succeeded in 1897 by *John A. Mandel* (1865–), who in 1901 invited *H. C. Jackson* (1875–), of Chittenden's laboratory at Yale, to be his assistant. The combination of the two men gave a strong department.

Charles Frederick Chandler (1836–1924) studied chemistry under Wöhler, took his Ph.D. degree in Göttingen in 1856, then accepted the position of janitor and assistant chemist at Union College in 1857, and became professor of chemistry there the following year. Between the years 1872 and 1897 he was professor of chemistry and medical jurisprudence at the College of Physicians and Surgeons in New York and a brilliant lecturer and teacher of undergraduates. In 1897 Columbia University invited Chittenden to superintend the installation of a department of physiological chemistry in their medical school. Chittenden established *William J. Gies* (1872–) in this institution to carry on and develop the traditions of the Yale laboratory.

Rudolf A. Witthaus (1846–1915), a proficient toxicologist, was professor of chemistry at the Cornell University Medical College between 1885 and 1911. He belonged to the old school of laboratory worker. He was succeeded by *Stanley R. Benedict* (1884–), a master of analytical technic. Benedict was a pupil of Mendel. He has discovered that the urine of the spotted coach hound contains uric acid, as in the case of man, and not allantoin, as in other varieties of dogs. He has found that the uric acid content of ox blood is wholly present in the corpuscles and occurs there in combination with a pentose. He has recently prepared from human and other bloods a new crystalline compound containing sulfur which he calls "thiasine." This is a substance which has long interfered with the accurate determination of uric acid in the blood by the colorimetric methods of Folin and of Benedict.

The United States is recognized as a leader in the development of new methods of rapid biological chemical analysis, and Otto Folin and Stanley Benedict are the dominant exponents of this art.

Victor C. Vaughan (1851–), long known as a most eminent toxicologist, was one of the earliest Americans to become interested in modern physiological chemistry. He attracted such men as W. H. Howell, J. J. Abel, and Arthur R. Cushny (1866–1926) to the University of Michigan and, because of his scientific knowledge, created there a medical school far in advance of its time. One of the men attracted thither was *Frederick G. Novy* (1864–), who has studied the chemistry of bacterial life, including the production of ptomaines and leucomaines. He has recently reported on the respiratory quotients developed by bacteria, pioneer work in this field.

Samuel J. Meltzer (Russia, 1851—New York, 1920), M.D., Berlin, 1882, was a man of the highest ideals, stimulating to thought and to action. His influence still lives in several societies which he founded. He discovered the anesthetic value of magnesium salts when they are injected into the spinal canal. His earlier years combined research with the practice of medicine, but the last years of his life were spent as a most honored member of the Rockefeller Institute for Medical Research.

With the advent of the great spirit of *Otto Folin* (1867–) in 1907, the Harvard Medical School grew in grandeur. Folin discovered a method for the ready determination of creatine and creatinine. He demonstrated that creatinine was a constant normal product of cellular metabolism and was uninfluenced by the amount of protein in the diet. He extended and more sharply defined the conception of an endogenous protein metabolism, as first enunciated by Burian. Especially celebrated is his "Laws Governing the Chemical Composition of Urine."[1] He was the first to follow to their destinations in the body amino acids orally administered.

It must not be thought that the last twenty-five years of the nineteenth century were devoid of accomplishment. At the centennial meeting of the International Medical Congress (1876) *Austin Flint, Jr.* (1837–1915), read a paper on "Experimental Researches into a New Excretory Function of the Liver." This work had been performed in 1862, had received honorable mention by the Académie des Sciences of Paris, and had been awarded a prize of 1500 francs. Flint demonstrated that biliary cholesterol is converted by bacterial action into a body called "stercorine,"

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[1] *Am. J. Physiol.*, **13**, 66 (1905).

in which form it appeared in the feces. The following quaint minute is culled from the record of the congress: "On motion the conclusions in Dr. Flint's paper were adopted as expressing the opinion of the section." The weight of Hoppe-Seyler's great name denied the validity of Flint's discovery, and it was not until Bondzynski in 1896 rediscovered stercorine that Flint's work was vindicated. With a not too delicate sense of scientific amenities, Bondzynski insisted upon retaining the name "koprosterin," which he had given to the compound isolated by him, even after Flint's priority had been established. Following this work of Flint his activity as an investigator lapsed, with the exception of some inaccurate calculations upon the effect of a six-day walk upon the protein metabolism of Weston.

Though there was no general influence making for better things during the last quarter of the nineteenth century, yet the years were not entirely barren. Thus, *Willard Gibbs* (1839–1903), of Yale, during the years 1874 to 1878 published articles in the *Proceedings of the Connecticut Academy* concerning the laws of surface tension and adsorption and the development of heat in the cell. These papers were translated into German by Ostwald in 1896 and presented by him to an astonished scientific world.

The Chemists in Biology

The founding of the Johns Hopkins University in 1876 was under the guiding influence of *Daniel C. Gilman* (1831–1908), who, when affiliated with the American diplomatic establishments in St. Petersburg and Berlin, had made a profound study of the systems of education in those countries. *Ira Remsen*, the discoverer of saccharin, was born in New York in 1846, received his M.D. at Columbia in 1867, Ph.D. at Göttingen in 1870, was assistant at Tübingen 1870 to 1872, was professor of chemistry at the Hopkins from 1876 to 1913, and president of the university from 1901 to 1913. With such men as Gilman and Remsen in control, it was not difficult to stimulate a young student who went to Baltimore in 1883 and who afterwards became the most outstanding individual among the chemists in physiology in America, *John J. Abel* (1857–). Abel studied in European universities between 1884 and 1890 (M.D., Strasbourg, 1888). Between 1890 and 1893 he taught pharmacology at the University of Michigan and then, in 1893, he became professor of pharmacology at the newly founded Johns Hopkins Medical School. He spent his summer holidays in European laboratories and had as his ideal the transplantation of the German scientific atmosphere into his own American laboratory. He has made many outstanding contributions. He prepared the blood pressure raising principle of the suprarenal capsules in the form of a benzoyl derivative and named the active substance "epinephrine." It was but a step for another to prepare the hormone itself, which was renamed "adrenaline." Abel was also the first to isolate a free amino acid (alanine) from the circulating blood. In recent years he, with his co-workers Rouiller and Geiling, has shown that the potency of a purified pituitary tartrate is such that maximal contractions of the virgin guinea-pig uterus are obtained when the substance is in dilution of 1:15,000,000,000. The latest announcement of Abel (1926) is that he has prepared pure crystalline insulin which gives the ordinary reactions for protein and contains an extremely labile sulfur group which is essential to the activity of the hormone. This substance, when given in doses of 0.01 milligram to the kilogram, reduces the blood-sugar level of the rabbit to the convulsive stage. It is "a hormone which in very high dilution influences carbohydrate metabolism, acting, as it were, like a catalyst in a chemical solution."

E. C. Kendall (1886–), a man of a later generation than Abel, has isolated thyroxin, the effective hormone of the thyroid gland, and has found that it contains 65 per cent of iodine. He believes that thyroxin incorporated into protoplasm functions as a catalyst. According to Kendall the activity of epinephrine and glutathione is of an analogous order.

These pieces of work stand in striking contrast to the welter of absurdity put forth by "clinical endocrinologists" and to the frauds of some of the pharmaceutical houses.

A pioneer in the field of pure chemical research is *Thomas B. Osborne* (New Haven, 1862–). He took his Ph.D. degree at Yale in 1885. Since 1886, as research chemist of the Connecticut Agricultural Experiment Station, he has been active first in the chemical analysis of various proteins and later (with Mendel) in the determination of their physiological importance. With infinite care he has determined the quantity of different amino acids contained in many varied proteins. He may properly be called the world's foremost authority on the chemistry of the vegetable proteins. This work was at first continued by *C. O. Johns* (1870–) and later by *D. Breese Jones* (1879–), a pupil of Osborne, at the United States Department of Agriculture, Washington, D. C.

Phoebus A. Levene (St. Petersburg, 1869–) migrated to this country in 1891 after receiving an M.D. degree at St. Petersburg.

Educated in many laboratories both in America and in Germany, he has been an inspiring influence at the Rockefeller Institute since its foundation. Here he for the first time determined the structural formula of nucleic acid, a problem the solution of which had evaded some of the world's master chemists. His work on the chemistry of mucoproteins shows that they contain conjugated sulfuric acid, and he has given a chemical formula for chondroitin sulfuric acid.

Henry D. Dakin (London, 1880–) came to this country about 1905. He has devoted his life to the study of the intermediary metabolism and to the oxidations and reductions in the animal body. He has made it probable that methyl glyoxal is an important and usual intermediary product in carbohydrate metabolism. He isolated β-hydroxyglutamic acid as a constituent of casein and has produced the substance synthetically. A careful investigator and a sound critic, his work has been beyond reproach.

Walter Jones (1865–) took his Ph.D. at the Johns Hopkins in 1891 and studied with Kossel at Marburg in 1899. He has made a lifelong and fruitful study of the nucleic acids and their derivatives. He has shown that the absence of guanase from the pig's liver prevents the transformation of guanine into xanthine and hence favors the production of guanine gout in the pig.

The Biological Chemists

Russell H. Chittenden (New Haven, 1856–) has rightly been called the "Grand Old Man of Physiological Chemistry in America." He received the degree of Ph.B. at Yale in 1875, worked with Kühne in Heidelberg in 1878 to 1879, was granted a Ph.D. from Yale in 1880, became professor of physiological chemistry there in 1882, and director of the Sheffield Scientific School in 1898. Denying himself all holidays, he worked unceasingly far past middle life in the fulfilment of that supreme mission, the preparation of young men to become teachers. His influence over them was phenomenal. Thus, he diverted Harvey Cushing from the contemplated study of architecture to the pursuit of medicine, and he gave to such men as Theodore C. Janeway, John Howland, and Elliott P. Joslin the touch of chemical insight necessary for the great clinicians which they became. They received a greater stimulus from his courses than was obtainable in the medical schools of their day. At his hands several great teachers received their doctorates, Lafayette B. Mendel, in 1893; William J. Gies, in 1897; Yandell Henderson, in 1898; Holmes C. Jackson, in 1899; Alfred N. Richards, in 1901; and Frank P. Underhill, in 1903. Also, H. Gideon Wells in 1893 received the degree of Ph.B. after work in his laboratory.

Chittenden's earlier work was concerned with the chemistry of protein, albumoses, and peptones. In 1875 he discovered glycogen and glycine in "scallops," the central muscle of *pecten irradians*. His most famous research was published in 1904 entitled, "Physiological Economy in Nutrition, with Special Reference to the Minimal Protein Requirement of the Healthy Man. An Experimental Study." In this he demonstrated that a man could live in vigorous health after taking half to a third the quantity of protein allowed in the standard diets of the period. On account of this work his name became well known in Germany and elsewhere in 1914 to 1918.

In 1898 he was called to administer the department of physiological chemistry in the medical school of Columbia University, New York City. He established a course there, placing his pupil, *William J. Gies* (1872–) in charge of most of the instruction, and in 1903 retired as head of the department, when Gies was placed in full control.

Lafayette B. Mendel (1872–), Ph.D., Yale, 1893, the most influential of all of Chittenden's pupils, studied also with Heidenhain at Breslau and with Baumann at Freiburg in 1895 and 1896, and on his return home became again closely associated with Chittenden, gradually relieving him of much of the direction of the laboratory work, especially after 1898 when Chittenden became director of the Sheffield Scientific School. Of the many scientific offspring of Mendel who hold academic positions, usually chairs of physiological chemistry, may be enumerated Robert E. Swain (Ph.D., 1904), Stanford University; Harold C. Bradley (Ph.D., 1905), University of Wisconsin; Tadasu Saiki (Ph.D., 1907), director, Nutrition Institute, Tokio; Stanley R. Benedict (Ph.D., 1908), Cornell University Medical College, New York City; Mary Swartz Rose (Ph.D., 1909), Columbia University; Victor C. Myers (Ph.D., 1909), University of Iowa; John F. Lyman (Ph.D., 1909), Ohio State University; William C. Rose (Ph.D., 1911), University of Illinois; Howard B. Lewis (Ph.D., 1913), University of Michigan; Ruth Wheeler (Ph.D., 1913), Nutrition, University of Iowa; Amy L. Daniels (Ph.D., 1914), Iowa; D. Wright Wilson (Ph.D., 1914), University of Pennsylvania; and Raymond L. Stehle (Ph.D., 1915), McGill University.

In this connection it should be recalled that E. V. McCollum took his Ph.D. degree under the chemist Treat B. Johnson at

Yale in 1906 and that he spent the academic year 1906–1907 in Mendel's laboratory.

Mendel's work has been prodigious in quantity, painstaking and accurate in quality. Always an omnivorous reader, a well-balanced critic, a sound adviser of men, and judge of the affairs of men, he has wielded a great and beneficent power upon his day and generation.

The bound reprints of the work of his laboratory constitute ten large volumes. At first his researches dealt largely with the metabolism of the purines, he then took part in the experiments of Chittenden on the protein minimum, and later, with T. B. Osborne, he developed the valuable line of investigation regarding the question as to what constitutes an adequate diet. The basis of this work was founded upon the growth curves of young rats, as influenced by diet, following a procedure originally adopted by Gowland Hopkins, of Cambridge, England. McCollum began similar experiments almost at the same time. The two sets of investigations have been somewhat at variance with each other, especially in the earlier years before the exact methods of analysis were clearly defined, but America may well be proud of the results obtained by both groups of workers.

Osborne and Mendel have clearly shown that rats grow and thrive when the protein contained in their diet is casein (devoid of glycine), whereas if the wheat protein, called "gliadin" (deficient in lysine), is substituted, body weight is barely maintained, and if the protein of Indian corn, called "zein" (devoid of glycine, lysine, and tryptophan), be given, even the maintenance of body weight is impossible. If the missing amino acids in the last two proteins are added to the food, normal growth is obtained.

Elmer V. McCollum (1878–), and independently Osborne and Mendel, discovered that growing rats, given a satisfactory diet, ceased to grow if lard were substituted for butter fat. And Osborne and Mendel reported that in the absence of butter fat an eye disease called "xerophthalmia" developed. Addition of butter fat to the diet caused renewed growth and cured the xerophthalmia. In Denmark during the World War butter fat was exported to Germany and cocoanut oil was substituted for it in the milk supply of the Danes to such an extent that malnutrition, stunting of growth, and xerophthalmia arose among the children. When the American work became known in Denmark the Danish government arranged to ration butter among the children and remedied the difficulty.

McCollum has given the letters of the alphabet to the various vitamins, pending the time when their composition shall be exactly determined. The one described above as being contained in butter fat is called "fat-soluble A." The vitamins may be described as follows:

Fat-soluble A, growth producing; antixerophthalmic.
Water-soluble B, antineuritic; appetite promoting.
Water-soluble C, antiscorbutic.
Fat-soluble (?) D, antirachitic.
Fat-soluble E, fertility promoting.

Given these factors as variants in the dietaries, as well as such factors as chemical differences in proteins, fats, and carbohydrates, it can well be imagined that an immense literature has grown up with regard to the dietetic influence of various foods. In his "Newer Knowledge of Nutrition" McCollum lists the special dietary properties of one hundred and sixty different materials which are commonly employed as foods. Though the work has been interesting and important, much of it still lacks the quantitative element which will appear when the different vitamins are isolated. The immensity and relative newness of the literature make the selection of salient points difficult.

Walter H. Eddy (1877–) and his associates report the preparation from yeast of "bios," which stimulates the growth of yeast and is perhaps the antineuritic vitamin B. It is a crystalline substance melting at 223° C., contains nitrogen, and is possibly a true "vit-amine."

In the study of pellagra *Joseph Goldberger* (Austria, 1874–) and *Carl Voegtlin* (Switzerland, 1879–) have been prominent, without effecting a definite solution of this problem. Voegtlin has also studied the effect upon the body of salvarsan and related arsenicals.

Alfred F. Hess (1875–) has made extensive investigations into the subject of infantile scurvy and has found the tomato to have effective curative properties and therefore to contain much of vitamin C. He was the first to discover that direct exposure of children to sunlight alone would cure rickets.

John Howland (1873–1926), professor of pediatrics at the Johns Hopkins Medical School, has made notable contributions to the physiological pathology of rickets. Working first with Marriott and then with Benjamin Kramer and Tisdale, he concluded that in uncomplicated human rickets there is a normal calcium content (10–11 mg. per 100 cc. of blood serum) of the blood but a low phosphate concentration. If the calcium of the blood falls below the normal in children, tetany ensues, tetany being due to a deficiency of the normal amount of calcium ions (7–5 mg. Ca per 100 cc. of blood serum). This corresponds with the previous discovery of *William G. MacCallum* (1874–) that the tetany following parathyroidectomy is due to a decrease in the calcium content of the blood.

The experimental proof by Raczynski in 1912 that deprivation of light in a puppy dog was the cause of rickets brought a host of interested workers into this field. Hess shortly afterward proved by X-ray examination of the bones that exposure to sunlight cured rickets in children.

McCollum, P. G. Shipley, and E. A. Park have induced rickets in rats when these animals were reared indoors on diets too low in either calcium or phosphorus. Rats do not develop tetany. But when the animals so treated had acquired rickets, the addition of cod liver to their rickets-producing ration, or mere exposure to ultra-violet radiation, or to sunlight itself, caused a return of the normal quantities of calcium and inorganic phosphorus in the blood serum and in consequence cured rickets. Finally, Howland, Kramer, and Shipley have found that when the rachitic cartilage of rats is suspended in a saline solution of calcium and phosphorus in the proportion found in normal blood, calcification occurs in the diseased tissue. Also, when rachitic cartilage is suspended in normal human serum, calcification occurs *in vitro*, but there is none when rachitic serum is used.

The rachitic vitamin D is undoubtedly a radioactive principle derived from sunlight. Thus, *Harry Steenbock* (1886–) found that irradiation with ultra-violet rays caused inactive vegetable oils to acquire antirachitic potency. He showed that the antirachitic potency of butter fat is due to the consumption by the mother of irradiated food materials, and Hess has discovered that irradiation of green vegetables and spinach increased their value in this regard.

Powers, Park, and Simmonds find that the radiant energy of the sun will not prevent the development of xerophthalmia in rats but delays its onset. They conclude that radiant energy very likely raises the level of cellular activity of the organism to the point where the onslaughts of disease are held for a time in check.

Herbert M. Evans (1882–), of California, has unveiled the presence of a fertility vitamin which he at first called "vitamin X," but which McCollum classifies as vitamin E. Evans found that when rats were reared on a standard diet wholly sufficient for their normal growth (casein 18, cornstarch 54, lard 15, butter fat

9, salts 4, with 0.5 gram yeast), they became sterile, both male and female. The unknown fertility-conferring factor was shown to be present in lettuce, meat, wheat germ, oats, alfalfa, and (sparingly) in milk fat, and is essentially different from vitamins A, B, C, and D. Very small amounts of wheat germ oil will restore fertility to the animals. Evans also reports that a specific "bios" contained in natural foods, such as wheat germ oil, is necessary for normal lactation.

Howard B. Lewis (1887–), a pupil of Mendel and now professor of biochemistry at the University of Michigan, has studied especially the metabolism of sulfur compounds in the body. He has found that the oxidation of sulfur in cystine cannot take place normally if the process of deamination is prevented.

William C. Rose (1887–), Ph.D., Yale, 1911, professor of biochemistry at the University of Illinois, has been interested in amino-acid chemistry and finds that arginine and histidine are not mutually interchangeable in the nutrition of animals, that arginine is not a precursor of creatinine, but that probably histidine is a precursor of the purines.

Carl P. Sherwin (1885–) received a degree of Sc.D. under Thierfelder at Tübingen in 1915. He and Thierfelder found that in man phenylacetic acid unites with glutamic acid to form phenylacetyl-glutamic instead of phenaceturic acid, as in the dog, and in this form appears in the urine. This was the beginning of much work upon the intermediary metabolism of aromatic compounds.

The Agricultural Experiment Stations

Samuel W. Johnson (1830–1909) was the son of a Connecticut farmer of old colonial ancestry. For many years he taught school and tried to save enough money to go to Germany to study scientific agriculture, there fostered by Liebig. His father reproved him for his fantastic ideas, but finally consented to give him in cash the equivalent value of that which he had given to his other children in lands, buildings, and farm stock. Writing his father in 1854 from Munich, he says he can live there for five hundred dollars a year and "when I think of Heidelberg and the great Bunsen; of Berlin and the glorious old Heinrich Rose—my heart, my stomach, something in that neighborhood, aches. I have just got to be able to appreciate and enjoy Germany."

In 1861 Johnson was lecturing on agricultural chemistry five times weekly at the Sheffield Scientific School, New Haven. Here W. O. Atwater became a pupil and afterward his private assistant. Through Johnson's influence the Connecticut legislature in 1875 had the honor of establishing at Middletown the first state agricultural experiment station in the United States, of which Atwater was placed in charge. In 1877 the legislature correctly defined it as existing "for the purpose of promoting agriculture by scientific investigation and experiment." At this time Johnson became its director. The other members of Johnson's staff at this, the model of all other similar state institutions in the country, were E. H. Jenkins and Henry Prentiss Armsby, both former pupils of Johnson. In 1886 T. B. Osborne joined the staff of the station and at Professor Johnson's desire began with the oat kernel to separate its protein constituents in a condition of purity. Osborne, who was Johnson's son-in-law, labored at these problems for many years. He was startled at one time to receive a German translation of his work.

Johnson's private library was a complete storehouse of scientific information on the subject of scientific agriculture. His pupils, Atwater and Armsby, achieved high distinction. And agricultural stations modeled on his own, that is, so ordered that appointments are free from political control, have reached high distinction.

The Pennsylvania State Agricultural College was established in 1859 under the presidency of *Evan Pugh* (1828–1864). A blacksmith in his youth, but inheriting a small fortune, he went abroad to study, and took a Ph.D. degree at Göttingen in 1856. He was an American associate of Johnson when he was in Germany. The college prospectus announced the ambition to become "the best agricultural college in the world," but the state refused adequate support. Even so great a scientist as *Henry Prentiss Armsby* (1853–1921) was terribly handicapped in his work by the niggardly support of the state. Armsby was trained under Johnson at Yale, receiving his Ph.D. there in 1879. The year of 1876 he spent at Leipzig. From 1887 until his death he was the outstanding personality at the Pennsylvania Agricultural Experiment Station. He built in 1902 the only calorimeter (Atwater-Rosa type) which has ever been successfully operated with large animals, such as cattle. His life's work was devoted to the study of the basal metabolism of cattle and the net energy value of the feeding stuffs on which they subsisted. The plan and execution of these researches, the best of their kind, are the monument of his life.

Calorimetry

William Olin Atwater (1844–1907), as has been said, was a pupil of Johnson at Yale. He obtained his Ph.D. in 1869 upon the basis of the first analyses of maize fodder made in this country, using modern methods. Between 1869 and 1871 he studied in Leipzig and Berlin.

Atwater became professor of chemistry at Wesleyan in 1873. He later (1888) became founder and chief of the Office of Experiment Stations, United States Department of Agriculture. Johnson writes of him then, "I have, with others, favored Atwater's appointment because he has the spirit of prophecy and appears to me to be a chosen vessel." Twenty-six years later his pupil, *Charles F. Langworthy* (1864–), at the time chief of nutrition investigations, United States Department of Agriculture, wrote in a private letter, "One of Professor Atwater's most marked characteristics was his almost prophetic insight into the needs and possibilities of nutrition investigation."

In 1887 Atwater spent some time in Voit's laboratory in Munich, where he came in close personal contact with Max Rubner, then Voit's first assistant. It was through these influences that he became interested in calorimetry. Rubner perfected his calorimeter for dogs in 1891. The Atwater-Rosa calorimeter for work on man was begun in 1892 and completed in 1897. Of the latter calorimeter Armsby wrote at the time, "By far the most important form of respiration-calorimeter yet devised, not only as regards accuracy but particularly in view of the range of the work of which it is capable, is that of Atwater and Rosa." Time has justified this eulogy.

Atwater and his associates were able to verify the law of the conservation of energy as applied to the human being. That is to say, they demonstrated that the quantity of heat produced by an individual during a given period is that quantity which can be derived from the energy liberated in the oxidation of food materials during the same period. The analytical tables of food materials prepared in 1899 by Atwater and Bryant have remained the standard work of reference since their publication and were eagerly sought in many countries during the war.

The cost of the calorimeter work was largely defrayed from United States government funds. Representative, afterward Senator, Morrill, of Vermont, was the farsighted individual most largely responsible for these grants. But money came from other sources, the state of Connecticut, the university at Middletown, and private subscriptions. The work on the calorimeter was a coöperative affair, but its signal success was undoubtedly due to the distinguished physicist, *E. B. Rosa* (1861–1921), then professor of physics at Wesleyan University and later chief physicist of the Bureau of Standards at Washington.

Just before Atwater's invalidism and death the Carnegie Institution of Washington agreed to endow the work and to build a special nutrition laboratory for him. Atwater especially desired to devise means to measure the oxygen consumption of a man while he was in the respiration-calorimeter. In this work he had the ardent support and assistance of a highly ingenious young assistant, F. G. Benedict, who succeeded him after his death.

Francis Gano Benedict (1870–) received his M.A. at Harvard in 1894 and a Ph.D. at Heidelberg in 1895. He joined Atwater's staff at Wesleyan in 1896 and was closely associated with him for ten years. In 1907 he was chosen director of the Carnegie Nutrition Laboratory at Boston.

One of the most striking pieces of work ever accomplished was Benedict's investigation into the metabolism of a fasting man. One hundred and twenty-five quantitative measurements of various kinds were daily recorded during a fasting period of thirty-one days.

Following Du Bois' lead, Benedict, out of the wealth of his statistical material, has given us standards for measuring the basal metabolism, i. e., the heat production of a person resting quietly in the postabsorptive state.

In association with *Elliott P. Joslin* (1869–), he has done much to promote a knowledge of the processes which go on in diabetes. And with *Fritz B. Talbot* (1878–) a long and very complete study has been made of the metabolism in children from infancy to maturity. This has given accurate standards. During the war Benedict made an important contribution to our knowledge regarding the relation between undernutrition and muscular efficiency. The body was shown to have a real measure of self-defense in that the basal metabolism falls rapidly under conditions of undernutrition, even though there be no great depletion of the protein reserves of the body.

Graham Lusk (1866–) received his Ph.B. in chemistry at Columbia University in 1887 and his Ph.D. from Baeyer in Munich in 1891. He lived in Munich for three years, two years of which time he spent in the research laboratory of Carl Voit.

At the Yale Medical School he discovered that the urinary dextrose-nitrogen ratio (the $D:N$ ratio of Minkowski) in the fasting and meat-fed dog under the influence of phlorhizin was usually 3.65, and later at the New York University and Bellevue Hospital Medical College he, with *A. R. Mandel* (1876–), established the same ratio for the totally diabetic man. S. R. Benedict found the same figures in a phlorhizinized man.

With *A. I. Ringer* (1883–) he determined the quantity of sugar yielded by various amino acids in metabolism. This work was later extended by Ringer when he went to the laboratory of physiological chemistry of A. E. Taylor at the University of Pennsylvania.

When called to the Cornell University Medical College in 1909 Lusk was given sufficient funds to build a respiration apparatus. John R. Murlin, who had been associated with him for six years, spent the early summer of 1909 with Benedict in the Carnegie Nutrition Laboratory at Boston. Here Murlin and *Thorne M. Carpenter* (1878–) investigated the energy metabolism of mothers and their children before and after birth. It was found that the heat production of the mother and new-born child was the same as that of the mother before parturition. The respiration-calorimeter was so near to perfection that it was decided to construct for the Cornell Medical College a duplicate for the measurement of the respiratory metabolism and the heat production of dogs and babies. For the project Dr. Benedict supplied an expert mechanic, and the whole undertaking was then put in the hands of *H. B. Williams* (1877–), now professor of physiology, Columbia University, who had a rare combination of attributes, being a physicist, a mechanic, a physician, as well as a medical scientist and a classical scholar. It was due to Williams' technic that John Howland was able to determine that a sleeping infant, six months old and weighing only 3 kilograms, absorbed 2.36 grams oxygen per hour, from which it was calculated that 7.71 kilocalories should have been produced, whereas 7.57 calories were actually measured by the calorimeter during the hour.

With this apparatus many experiments have been carried out on dogs in the study of the behavior of various foods and individual metabolites.

In this same laboratory *John R. Murlin* (1874–), working with H. C. Bailey, showed that the heat production of new-born babies was exceedingly low for their size. Here, also, he worked for many months upon the all-engrossing problem of the effect of pancreatic extracts on pancreas diabetes. In 1913 he and Benjamin Kramer actually had a potent boiled extract of the pancreas in their hands, one that caused an oxidation of glucose in a depancreatized diabetic dog, as determined by an increase in the respiratory quotient. The year previous to this *Ernest Lyman Scott* (1877–), in Carlson's laboratory, prepared an extract from the pancreas which greatly reduced the *D:N* ratio in a completely depancreatized dog. These were the two outstanding

American contributions of the pre-insulin period of diabetic glandular therapy.

During the war Murlin became Lieutenant Colonel in the Sanitary Corps, and between 1917 and 1919 he was director of the Division of Food and Nutrition, Medical Department, U. S. A. Under him were marshalled Carlson, Shaffer, Woodyatt, Gephart, and many others whose business it was to improve the quality of the food and diminish its waste in Army cantonments and in the field. And the task was well done.

Rudolph J. Anderson (Sweden, 1879–), B.S. at Tulane, 1906; did graduate work at Upsala, London, and with Emil Fischer at Berlin; took his Ph.D. at Cornell, 1919. Some work with Lusk showed conclusively that the energy production in a fasting dog during a period of running at a rate of three miles per hour was exclusively derived from the oxidation of fat, as indicated by a non-protein respiratory quotient of 0.713 on the thirteenth day of the fast. He has studied the phytosterols of vegetable oils. He has found that the coloring matter of Norton and Concord grapes consists of a glucoside, anthocyanin.

The Russell Sage Institute of Pathology, through the use of its comparatively small funds, established a respiration-calorimeter in Bellevue Hospital, New York City, the success of which is directly attributable to its medical director, *Eugene F. Du Bois* (1882–). For the first time a respiration-calorimeter was built in a hospital and this was done in a city-owned hospital. The undertaking was under the control of a full-time staff. Here accurate normal standards of basal metabolism for people in good health were for the first time established. The difference between these standards and those afterwards given out by Benedict is slight. If the general average of metabolism tests is taken, Du Bois' values are more likely to be right than Benedict's. If the lowest of three observations is accepted as the basal value of metabolism, then Benedict's tables should be used.

After establishing basal values in normal people, Du Bois and *Warren Coleman* (1869–) investigated the metabolism of patients suffering from typhoid fever, extending the knowledge of the "high calorie diet" originally commended by Warren Coleman and Philip A. Shaffer. This work, together with one on malarial fever by Du Bois and *David P. Barr* (1889–), now professor of medicine, Washington University, St. Louis, presented a most complete record of the heat production and the heat loss during fever. It was found that in malarial chill the evaporation of water remained at its former level, that the heat loss by radiation and conduction was unchanged, and that all the extra heat produced by the muscular activity of shivering during the chill was stored in the body, raising its temperature accordingly.

Du Bois also made important studies on exophthalmic goiter. With *Frederick M. Allen* (1879–) and with *J. C. Aub* (1890–), working on diabetic patients of record severity, much was learned. In one instance it was discovered that a potentially diabetic man, whose urine was made free from sugar by dieting, was converted into a completely diabetic individual with a $D:N$ ratio of about 3.65 on the second day of a diet containing fat and much protein.

William S. McCann (1889–), now professor of medicine, Rochester University, New York, and D. P. Barr made use of the calorimeter in the investigation of tuberculosis. They found that a large protein intake increased the metabolism as in normal men, and since this results in increasing respiratory movement, a limited protein intake was recommended to put the lungs at rest. The food requirements of the tuberculous patient were found not to be large, and forced feeding they believed to be unnecessary and harmful.

James H. Means (1885–), of the Harvard Medical School, has shown that as a rule the metabolism in obesity conforms to the normal surface area standards.

Francis W. Peabody (1881–), professor of medicine at the Harvard Medical School and physician to the Boston City Hospital, has made important contributions to knowledge concerning acidosis and dyspnea in renal and cardiac disease and (with A. L. Meyer and Du Bois) has shown that, although the metabolism is often increased in these conditions, yet the quality of the metabolism remains quite as under normal conditions, as indicated by the respiratory quotients revealed.

In 1912 it was said of the United States that, although physiological chemistry and biology flourished here as nowhere else, yet the country was singularly barren in the field of scientific masters of medicine. The whole aspect of affairs has changed within the last decade and largely through those who have followed biochemical work. It may be of note that when John Howland was a practicing physician in New York he met Du Bois, then just out of an internship at the Presbyterian Hospital, and advised him to abandon bacteriology, which he planned to study in Germany, and turn to chemistry.

Attention has already been called to the work of Joslin, Lusk, Scott, Murlin, and others upon the subject of diabetes. Frederick

M. Allen, at the Rockefeller Institute, recommended complete fasting as a remedy for diabetes. This was a more drastic application of the principle of undernutrition recommended by Naunyn. Both *Henry R. Geyelin* (1884–) and *Isidor Greenwald* (1887–) have reported cases of complete human diabetes in which the *D*:*N* ratio on a meat-fat diet approximates 3.65:1.

The question of the occurrence and disappearance of the acetone bodies in diabetes is one which has occupied the interest of several American investigators. The first philosophical consideration of this subject was by *Rollin T. Woodyatt* (1878–) in 1910, who wrote concerning the possibility of certain metabolites of sugar reacting to produce the oxidation of β-oxybutyric acid. He gave glycolaldehyde to a diabetic dog and saw that it was antiketogenic, i. e., prevented the production of β-oxybutyric and acetoacetic acids. These acids are the end products of the oxidation of fatty acids, palmitic acid, for example. A. I. Ringer suggested in 1913 that acetaldehyde, believed to be produced in carbohydrate metabolism, united chemically with β-hydroxybutyric acid in the normal organism, enabling a final oxidation of the substance.

It is illuminating to compare the statement of Rosenfeld in 1885, "The fats burn in the fire of carbohydrate," with that of Woodyatt in 1916, "When the mixture of metabolites oxidizing in the body contain more than three molecules of higher fatty acid" (plus one of glycerol) "to one of glucose, then the body 'smokes' with acidosis compounds like an automobile with too much oil in the cylinders."

Woodyatt has demonstrated that to be certainly free from acidosis in practice an individual must have at least 1 gram of glucose to provide for the normal oxidation of 1.5 grams of fatty acid. Such a relation is found in a diet made up of protein, 50 grams; carbohydrate, 57 grams; and fat, 139 grams. In making the computation one must remember that fat yields 10 per cent of glycerol (a glucose derivative), and protein yields 58 per cent of glucose and 54 per cent of fatty acid.

Philip A. Shaffer (1881–), the distinguished pupil of Folin and professor of physiological chemistry at Washington University, St. Louis, has shown *in vitro* that acetoacetic acid in alkaline solution is not oxidized by peroxide of hydrogen, but that if glucose or glycolaldehyde be added to the solution, complete oxidation follows, just as occurs *in vivo*. Shaffer has also made most beautiful calculations of the millimols of glucose and of the millimols of fatty acid which were oxidized together in the mixture of metabolites, as calculated from various published metabolism experiments. In 1922 he concluded that the presence of one molecule of glucose was sufficient to cause the proper and complete oxidation of two molecules of fatty acid.

The rationale of the high fat diet of *Louis H. Newburgh* (1883–) is based on supplying the caloric needs of the body of the diabetic with a diet low in protein, high in fat, and with just enough carbohydrate to prevent the appearance of acetone bodies in the urine.

Such may be the useful practical results of the cultivation of pure theoretical science. Of the men engaged in this development Woodyatt and Ringer have worked in the clinic of Friedrich Müller, in Munich; Newburgh with Eppinger, in Vienna; and Du Bois with Kraus, in Berlin. There must exist an "atmosphere" to promote scientific enthusiasm.

Walter M. Boothby (1880–) has accomplished interesting work at the Mayo Clinic. After injecting a myxedematous patient, whose basal metabolism was 30 per cent below normal, with 16 milligrams of Kendall's thyroxin, an increased heat production of 16,125 calories occurred during the following six weeks over and above the quantity this patient would otherwise have produced. Boothby made a similar analysis of the action of epinephrine. He calculates that, whereas 1 milligram of thyroxin induces an extra heat production of 1008 calories, 1 milligram of epinephrine increases the basal metabolism only 50 calories. A molecule of thyroxin is stated to be sixty-four times more potent than one of epinephrine.

Joseph C. Aub (1890–) and his associates at the Harvard Medical School have demonstrated that the action of thyroxin upon the metabolism of cats is not influenced by the presence of the adrenal glands; and also that the 25 per cent fall in the metabolism of cats after the removal of the adrenals takes place whether the thyroid is present or not. He has also studied intensively the subject of lead poisoning.

David Marine (1880–) demonstrated in 1917 that the prophylactic administration of small amounts of sodium iodide to the school children of Akron, Ohio, a district in which goiter was prevalent, prevented a goitrous enlargement of the thyroid in over 99 per cent of the children treated. The demonstration was on a very extended scale.

The Chemistry of the Blood

William Henry Howell (1860–), the distinguished professor of physiology at the Johns Hopkins Medical School, has separated thrombin from its union with fibrinogen and found that it is thermostable in boiling water, is free from calcium, and will form a chemical union with fibrinogen to form fibrin. According to Howell, antithrombin present in the fresh blood prevents calcium salts from converting prothrombin into thrombin. Howell has also advanced evidence to show that the inhibition of the heart following the stimulation of the vagus is due to the liberation of potassium ions. And he was the first to discover a pressor substance in extracts of the posterior lobe of the pituitary gland.

The modern knowledge of the acid-base equilibrium of the blood was first placed before us by *Lawrence J. Henderson* (1878-), of Harvard University. He has also dealt in masterful manner with the philosophy of science.

Frank C. Mann (1887-), of the Mayo Foundation, with extraordinary skill, has devised a method for extirpating the liver in dogs, and finds that in the absence of this organ the regulation of the blood sugar is lost; the blood sugar falls to the level which produces convulsions. Injections of glucose for a time remedy the condition. He has shown conclusively that the seat of urea formation is in the liver and that the oxidation of uric acid to allantoin takes place there also. Furthermore, that the bile pigments arise in the bone marrow and in the spleen.

Donald D. Van Slyke (1883-), a pupil of Levene, has labored for many years upon the tension of gases in the blood. He was the first to devise a method for the direct determination of amino acids in the blood and tissues. He also invented an apparatus for the easy measurement of the CO_2-combining power of the blood and showed that the fall in this combining power was directly proportional to the intensity of acidosis in diabetes and in other diseased conditions. Many men have been carefully trained under his guidance and stimulated to correct scientific behavior by his painstaking thoroughness.

Walter R. Bloor (Canada, 1877-) obtained his Ph.D. at Harvard in 1911 under Folin and is one of his most eminent pupils. He is now professor of biochemistry at the University of Rochester, Rochester, New York. Bloor has especially investigated the time relations of the absorption of fat into the blood stream and has analyzed the distribution of lipoids in the blood in health and in diabetes, anemia, nephritis, etc., separately determining in whole blood, plasma, and corpuscles the content of total fatty acid, fat, lecithin, and cholesterol. He is a master of the chemistry of the lipoids.

Anton J. Carlson (1875-), the eminent physiologist of the

University of Chicago, has invaded the field of chemistry in his contributions on the control of hunger in health and disease, especially as regards the composition of the gastric juice.

The Function of Organs

Charles C. Guthrie (1880–), of the University of Pittsburgh (with Carrel as his pupil), was a pioneer in the work of transplanting organs. It was he who removed a kidney and transplanted it in the neck. The kidney, thus isolated and supplied with carotid blood, functioned perfectly.

Alfred N. Richards (1876–), professor of pharmacology at the University of Pennsylvania, has introduced a micro-pipette into an individual glomerulus of a frog's kidney and, using microchemical methods, has found that the composition of the glomerular filtrate is almost the same as that of the blood.

Jacques Loeb (1859–1925), the noted biologist of the Rockefeller Institute, was first to develop free swimming larvae from the unfertilized eggs of sea urchins through treatment of the eggs with certain saline solutions. He called the process "artificial parthenogenesis."

Loeb demonstrated that the laws of general chemistry hold true for protein, that the error of the colloid chemists lay in their lack of consideration of the hydrogen-ion concentration of their solutions, and that they investigated proteins in the presence of an excess of electrolytes. "The Dynamics of Living Matter," published in 1906, was an early masterpiece and included his studies on tropisms. He stimulated a great group of co-workers and was inspired with genius and true greatness.

William Mansfield Clark (1884–) received his Ph.D. at the Johns Hopkins in 1910. He devised methods for the study of the influence of hydrogen-ion concentrations upon bacterial metabolism. He has studied the growth optima of bacteria in relation to the hydrogen-ion concentration of the fluids in which they develop.

Albert P. Mathews (1871–) was with Kossel in Marburg in 1895 to 1897, and received his Ph.D. at Columbia in 1898. He is professor of physiological chemistry at Cincinnati. He has contributed much to chemical theory and has written a textbook on physiological chemistry which ranks as the best of its kind.

Martin H. Fischer (Germany, 1879–), M.D., Rush, 1901, has been professor of physiology at Cincinnati since 1910. His books, one on the theory of nephritis and the other on edema, have attracted world-wide attention.

G. H. A. Clowes (England, 1877–), Ph.D., Göttingen, 1899, is research director of Eli Lilly & Company, a physical chemist of high repute, whose scientific knowledge was largely contributory to the commercial preparation of insulin on a large scale.

Edmund N. Harvey (1887–), of Princeton University, demonstrated that the production of light by the firefly is due to oxidation. He dried the photogenic organ of the firefly *in vacuo* and found that it would emit light by the addition of water containing oxygen.

Public Welfare

It would seem that biological chemistry best serves the people through its aid to agriculture and through nutrition. The country is greatly indebted to *Harvey W. Wiley* (1844–) for the passage of the pure food laws. His successor, *Carl L. Alsberg* (1877–), who studied at Strasbourg under Schmiedeberg, contributed greatly to the scientific distinction of the important position of chief chemist of the United States Department of Agriculture. After the United States entered the war *Herbert Hoover* (1874–), head of the Commission for Relief in Belgium, organized the United States Food Administration. *Alonzo E. Taylor* (1870–), one of the early pupils of Arrhenius, and formerly professor of physiological chemistry of the University of Pennsylvania, a man of high scientific attainments, became Hoover's principal scientific adviser. He was also a member of the important War Trade Board. Chittenden and Lusk were sent abroad by Hoover in the winter of 1918 as members of the Interallied Scientific Food Commission, and the following autumn Mendel and Armsby went on the same mission. The problem was to solve the way to nourish a population of 225 million people on scientific principles.

The education of the masses upon the question of home economics has been widespread in the United States, and especial emphasis has always been placed upon the subject of nutrition. *Henry C. Sherman* (1875–), who was early associated with Atwater and now for many years with Columbia University, has been one of those through whose investigations, writings, teachings, and pupils this knowledge has been constantly promoted. He has found the requirement of calcium in the diet of an adult to be 0.42 gram per day and he has never ceased the advocacy of a large intake of milk to cover this requirement.

Women such as *Isabel Bevier, Helen Atwater, Ellen H. Richards, Amy L. Daniels, Mary Swartz Rose, Grace MacLeod,* and *Katharine Blunt* have fixed dietary standards for women and children on the basis of metabolism studies which have great value. And they have carried the torch of learning into the home itself.

Conclusion

It would seem unfriendly in conclusion not to mention our friends and neighbors, A. B. Macallum, a great original pioneer, Macleod, Banting, Collip, and Andrew Hunter, who across the great border of the Dominion of Canada have contributed largely to inspire our own work.

In reviewing this brief and incomplete summary of American contributions to physiological chemistry, the part that Germany has played in educating American scientists stands out strongly. It is a question whether we, in the United States, are not really living in the reflected glory of another country which has been exported hither, but which we cannot develop properly in succeeding generations. Is our own intellectual sustenance really an adequate diet containing the proper building stones and the fertility vitamin E? Are we now on the crest of productivity or are we just beginning? As to this, the next half-century of the AMERICAN CHEMICAL SOCIETY will bear witness.

During the winter of 1898–1899 a few men met at one another's homes in New York and became acquainted. These were J. K. Thatcher, Christian Herter, E. K. Dunham, Frederic Lee, Benjamin Moore (late professor of biological chemistry at Oxford), W. H. Park, and Graham Lusk. About 1902 a small group formed a journal club on biological chemistry which met at the Bellevue Medical College, because it was the only medical college whose doors could then be opened in the evening, and, after hearing papers, partook of beer and sandwiches. Here were to be found Levene, John Mandel, Horst Oertel, George Wallace, Jackson, Gies, E. K. Dunham, A. N. Richards, and Lusk. Here lifelong friendships were formed. It seems in retrospect like the origin of all things in New York. It is a parochial story. But the same kind of gatherings were then beginning or were in their infancy all over the country; helpful and stimulating they were, both at that time and throughout the lives of the individuals affected. For progress is deeply interwoven with human contacts.

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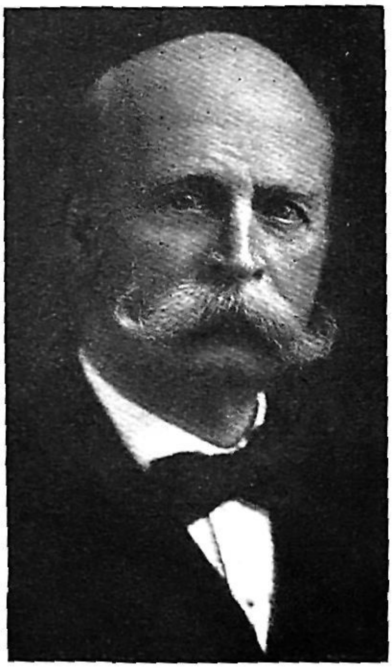

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(1874-)
Treasurer, 1919-

CHAPTER XI

AGRICULTURAL CHEMISTRY

BY CHARLES A. BROWNE

The Early Workers

Chemistry and agriculture have maintained a close relationship in America from the very beginning. The earliest chemist of the English Colonies, John Winthrop, Jr., first Governor of Connecticut, was greatly interested in agriculture and in 1663 read a paper upon the "Description, Culture and Use of Maize" before the Royal Society, of which he was a member. From the date of this early contribution the records of agricultural chemistry in America are almost continuous.

The importance of chemistry to agriculture was clearly realized by the founders of our Republic. Thomas Jefferson, during his presidency, and John Adams, during his retirement upon a farm at Quincy, recommended in almost identical words the pursuit of chemistry in so far as it helped to produce better bread, butter, cheese, beer, wine, cider, gardens, orchards, and fields, but they both expressed themselves as unfavorable to the study of chemical theories. This stress upon the practically useful appears also in many American textbooks of the early nineteenth century which dwell constantly upon the parts of chemistry of most utility to farmers, mechanics, and housewives. But notwithstanding some excellent features in the works of Thomas Ewell, Amos Eaton, Edmund Ruffin, Samuel Dana, and other writers of this period, agricultural chemistry in America, as in other parts of the world, wandered aimlessly about until 1840 when it was set definitely upon the right path with the publication of Liebig's "Chemistry in Its Applications to Agriculture and Physiology."

EBEN N. HORSFORD.—The earliest of Liebig's American students to promulgate his master's teachings was Eben N. Horsford (1818–1893), who published in 1846 his "Chemical Essays Relating to Agriculture." In 1847 he became Rumford professor of chemistry at Harvard and exerted a great influence upon chemistry in America during the next forty years. He was greatly interested in the chemistry of foods, as is shown by his "Theory and Art of Breadmaking," published in 1861, and by his technical processes for manufacturing baking powder and condensed milk. He was one of the chemists who attended the Priestley Centennial at Northumberland in 1874 and later he became a member of the AMERICAN CHEMICAL SOCIETY. His diversified activities as teacher, manufacturer, and antiquarian brought Professor Horsford a greater degree of popular celebrity than was achieved by any American chemist of his day.

ST. JULIEN RAVENEL.—Members of the medical profession have always played a conspicuous part in agricultural chemistry in America, and prominent among these should be mentioned St. Julien Ravenel (1819–1882), of Charleston, South Carolina, the descendant of French Huguenot pioneers. He graduated from the Medical College of South Carolina in 1840 and, after completing his studies in Philadelphia and Paris, returned to Charleston to take up the practice of medicine. In 1852 he retired from medical practice in order to devote his attention to the applications of chemistry to agriculture. He visited the marl bluffs on Cooper River in 1856 and, ascertaining that this rock could be converted into lime, established kilns which furnished most of the lime used in the Confederate States. During the Civil War Dr. Ravenel was surgeon-in-chief of the Confederate hospital in Columbia and director of the Confederate laboratory in that city for the manufacture of medical supplies. He was the first to realize the immense agricultural importance of the phosphate rocks of South Carolina, and his experiments upon the transformation of these deposits into commercial fertilizers marked the dawn of the mineral phosphate industry of the South. He founded the Wando Phosphate Company for the manufacture of fertilizers and conducted extensive field tests upon the application of fertilizers to crops. He also made an agricultural chemical survey of the rich alluvial rice lands of his native state. Dr. Ravenel was especially distinguished for his philanthropic services in various outbreaks of yellow fever and his name is still revered in many places that were visited by this epidemic. The following tribute was paid to him in 1882, at the time of his death, by Charles Upham Shepard, Jr.:

> Well might this community erect a public monument in honor of the man to whom preeminently is due the inauguration of that phosphate industry

which has proven of such incalculable value to ourselves and others. As the statue of Berzelius adorns beautiful Stockholm, let us commemorate the founder of Charleston's greatest industry.

JOHN P. NORTON.—Two brilliant young scientists, John P. Norton (1822–1852) and Evan Pugh (1828–1864), upon returning from their European studies, gave a great impetus to the study of agricultural chemistry in America. In 1847 Norton was appointed professor of agriculture at the Yale Scientific School and during this connection published in 1850 his "Elements of Scientific Agriculture," which was awarded a prize by the New York State Agricultural Society. Until his early death at thirty Norton distinguished himself as a copious writer upon agricultural subjects and as an inspiring teacher.

EVAN PUGH.—Dr. Pugh is best known for his famous research upon the "Sources of the Nitrogen of Vegetables," which was conducted during 1857–1859 in the laboratory of Lawes and Gilbert at the Rothamsted Agricultural Experiment Station in England. He returned to the United States in 1859 to accept the presidency of the Pennsylvania Agricultural College and died in this office five years later at the age of thirty-six. In the early deaths of two such investigators as Norton and Pugh, American agricultural chemistry suffered a most serious loss.

SAMUEL W. JOHNSON.—The most potent influence in early American agricultural chemistry was Samuel W. Johnson (1830–1909), third President of the AMERICAN CHEMICAL SOCIETY, whose youthful essay in 1847 upon "Fixing Ammonia" gave promise of the man. He was inspired to make agricultural chemistry his life work by his teacher, J. P. Norton, at Yale during 1850 and 1851. After returning from his European studies under Liebig, young Johnson was appointed professor of analytical chemistry at the Yale Scientific School in 1856. The subject of agricultural chemistry was added to his professorship in 1857 and this became the central activity of his career during the next fifty years. Seven books and one hundred and seventy-two articles upon agriculture and agricultural chemistry are among the evidences of his industry. His lectures and publications upon soils, rotation of crops, fertilizers, methods of analysis, plant nutrition, food adulteration, and many other subjects exerted a great influence upon the development of scientific agriculture in America. By beginning in 1856 a systematic chemical examination of the commercial fertilizers which were sold in Connecticut, Johnson became the founder of agricultural regulatory work in America. He was largely instrumental in securing the passage of the Connecticut law of 1869 which, although imperfect, was the first that required fertilizers to be labeled with a statement of composition, thus helping to fulfil the prophecy of his teacher, Liebig, that the time would come when no artificial manure would be sold whose exact amount of efficacious ingredients was not known.

A most important event in the history of agricultural chemistry in America during the past fifty years was the establishment of the State Agricultural Experiment Stations, and in the early stages of this movement Johnson was the undisputed leader. For many years he had advocated the establishment of a State Agricultural Experiment Station, but it was not until 1875 that Connecticut made its first attempt with private financial support to found an institution of this kind at Middletown with W. O. Atwater (1844–1907), a former pupil and assistant of Johnson, as director. Two years later Connecticut reorganized its experiment station as a wholly independent state institution in New Haven with Johnson as director. The Connecticut Agricultural Experiment Station, of which the fiftieth anniversary was celebrated on October 12, 1925, was instrumental in training many chemists who afterwards became directors of experiment stations in other states, when their establishment was made possible by federal support under the Hatch Act of 1887. H. P. Armsby, director of the Pennsylvania station; E. H. Jenkins, director of the Connecticut station; W. H. Jordan, director of the Maine and later of the New York station at Geneva; A. T. Neale, director of the Delaware station; and C. D. Woods, director of the Maine station, all obtained their early agricultural chemical training in Connecticut, either at Middletown or New Haven.

Johnson was an excellent critic of agricultural chemical work and, while himself making no contributions of striking originality, he performed a lasting service in the two classic volumes, "How Crops Feed" and "How Crops Grow," by winnowing the essential truths of the science from the chaff which had accumulated from preceding generations. These works have been translated into many foreign languages. Professor Johnson is also to be remembered for his well-known translations of the famous manuals of Fresenius by which many American chemists obtained their introduction to qualitative and quantitative analysis.

CHARLES A. GOESSMANN.—Next to S. W. Johnson the leading influence in American agricultural chemistry fifty years ago was Charles A. Goessmann (1827–1910), President of the AMERICAN CHEMICAL SOCIETY in 1887. The interests and activities of these two men ran parallel in many ways. Goessmann was born at

Fritzlar, Germany, and after taking his doctor's degree at Göttingen in 1852, served five years as assistant at this university under his teacher, Friedrich Wöhler. The publication in 1854 of a paper upon his newly discovered arachidic acid attracted immediate attention. Numerous contributions upon the composition of vegetable oils and other plant constituents followed in rapid succession.

Among those whom Goessmann taught at Göttingen were the American students G. C. Caldwell, C. F. Chandler, W. S. Clark, John Dean, E. P. Eastwick, J. H. Eastwick, S. S. Garrigues, J. D. Hague, Edward Hungerford, C. A. Joy, J. F. Magee, J. W. Mallet, Ebenezer Marsh, H. P. Nason, Evan Pugh, D. K. Tuttle, and G. W. Weyman. Including Goessmann himself there were in this group five future Presidents and five Charter Members of the AMERICAN CHEMICAL SOCIETY.

In 1857 Goessmann was persuaded by his former students, the Eastwick brothers, to become the chemist and superintendent of their sugar refinery in Philadelphia. After eleven years of technical activity in the United States with sugar and salt industries Goessmann accepted in 1868 the professorship of chemistry at the Massachusetts Agricultural College at Amherst. In 1882 he was also appointed director and chemist of the newly established Massachusetts Agricultural Experiment Station. Until his retirement in 1907 Goessmann published three hundred and sixty-two chemical papers and reports. His contributions upon soils, fertilizers, tillage, sugar cane, sugar beets, sorghum, fruits, ensilage, cattle feeding, dairy products, etc., cover the whole range of the applications of chemistry to agriculture, and his researches gave a strong impress to the character of the work which many American agricultural experiment stations took up in the early years following their establishment. Largely as a result of Goessmann's activities, the Legislature of Massachusetts passed the first effective state laws for controlling the purity of fertilizers and feeding stuffs.

Goessmann, like Johnson, exerted a great influence, through his pupils, upon the future of agricultural research in America. He foresaw the importance of the agricultural chemical investigations of Henneberg, Tollens, and others of the Göttingen school and he encouraged not only his own graduates but others to complete their scientific training at this university. The drift of young American chemists to the Agricultural Institute of Göttingen continued unslackened until the World War; E. W. Allen, C. A. Browne, W. B. Ellett, E. R. Flint, J. B. Lindsay, T. L. Lyon,

B. B. Ross, H. E. Stockbridge, W. E. Stone, Charles Wellington, H. J. Wheeler, J. A. Widtsoe, F. W. Woll, P. A. Yoder, and many others participated in this movement.

ROBERT C. KEDZIE.—Another early pioneer in American agricultural chemistry was Robert C. Kedzie (1823–1902). After graduating from Oberlin College in 1846 and from the Michigan State University Medical School in 1851 he practiced medicine until 1861. He then entered the Army to serve as surgeon in the Civil War, but resigned in 1863 to accept the professorship of chemistry at the Michigan Agricultural College where he taught until his death. In addition to his long services as a teacher of agricultural chemistry, Dr. Kedzie did a large amount of practical experimental work that was of great value to the farmers of his state. He studied the muck lands and other soils of Michigan, investigated the importance of the volatile constituents of animal manures to crop growth, and made experiments upon the fertilizing action of wood ashes, lime, land plaster, and salt. The Michigan fertilizer law was largely the result of his labors, as were also various other enactments for protecting the public welfare. His crusades against adulteration and other frauds were conducted with persistence and vigor. His investigations upon the chemical composition and baking quality of Clawson wheat were of great value to Michigan farmers. He was the first to grow sugar beets in Michigan and the Michigan beet sugar industry owes its origin to him. Dr. Kedzie was one of the group of chemists who attended the Priestley Centennial at Northumberland in 1874. He took an active part in the work of the Association of Official Agricultural Chemists, and was president of that organization in 1899.

NATHANIEL T. LUPTON.—Nathaniel T. Lupton (1830–1893) should also be mentioned as one of the more prominent early agricultural chemists of America. He was born at Winchester, Virginia, and obtained his collegiate training at Dickinson College, Pennsylvania, where he received the M.A. degree in 1849. After teaching for a number of years he took a postgraduate course in chemistry under Bunsen at Heidelberg. During the Civil War he was chemist in the Ordnance Department of the Confederate Government at Selma, Alabama, where he supervised the manufacture of powder. After the war he became professor of chemistry at the University of Alabama, of which he was president from 1871 to 1874. From 1875 to 1885 he was professor of chemistry at Vanderbilt University. In 1885 he was appointed professor of chemistry at the Alabama Polytechnic Institute and state chemist of Alabama, retaining these positions until his death. He published his "Elementary Principles of Scientific Agriculture" in 1880 and was president of the Association of Official Agricultural Chemists in 1892.

FRANCIS H. STORER.—Two other chemists of the older generation, who exerted a great influence upon the development of agricultural chemistry in America, were F. H. Storer (1832–1914) and E. W. Hilgard (1833–1916). Their work, although of very different character and in widely separated states, was closely contemporaneous. Storer obtained his first training in chemistry at Harvard, where he graduated in 1855. After returning from two years' postgraduate study in France and Germany he occupied various positions as consulting chemist and teacher until 1870, when he was appointed professor of agricultural chemistry at Harvard. In the following year Storer was made dean of the Bussey Institution of Harvard and he retained these two offices during the rest of his active career. He published numerous papers upon fertilizers, fodders, foods, wood, and other agricultural chemical subjects. Professor Storer is best known for his three-volume treatise, "Agriculture in Some of Its Relations with Chemistry." He also published "First Outlines of a Dictionary of Solubilities of Chemical Substances" and a "Cyclopedia of Quantitative Chemical Analysis."

EUGENE W. HILGARD.—E. W. Hilgard was born in Bavaria and came to the United States with his parents when only three years of age. After attending the public schools of southern Illinois he studied abroad at Zürich, Freiberg, and Heidelberg, receiving the degree of Ph.D. at the last-named university in 1853. In 1855 he became chemist of the Smithsonian Institution but soon resigned this office to conduct geological studies in Mississippi, where he was state geologist from 1858 to 1872. It was during this period that he began his epoch-making investigations upon the chemical composition and geological formation of soils. Hilgard occupied the chair of geology at the University of Michigan from 1873 to 1875, when he was appointed professor of agriculture at the University of California. He was also made director of the California Agricultural Experiment Station and continued actively in the work of these positions until his retirement in 1909. Hilgard's studies of the soils of the humid and arid regions of the United States in their chemical, physical, and geological relationships to agriculture laid the foundation of modern soil science. He prepared a report on the soils of the cotton-growing states for the Tenth Census. His treatise on "The Relations of

Soil to Climate," published by the United States Department of Agriculture in 1892, was reprinted in both France and Germany. A later volume upon "Soils," comprising the results of his extensive life studies in this field, was published in 1906. Hilgard was one of the group of chemists who attended the Priestley Centennial in 1874.

GEORGE C. CALDWELL.—Another prominent chemist, influential in helping to lay the foundations of agricultural chemistry in America, was G. C. Caldwell (1834–1907), President of the AMERICAN CHEMICAL SOCIETY in 1892. He obtained his first instruction in chemistry at Harvard University from which he graduated in 1855. After attending the College of Agriculture at Cirencester, England, he studied under Wöhler and Goessmann at Göttingen University where he obtained his doctor's degree in 1857. Upon returning to the United States he taught chemistry at the Pennsylvania State College of Agriculture, of which he became vice president. In 1867 he was appointed professor of agricultural chemistry at Cornell University, which had just been founded. He afterwards became head of the Chemical Department of Cornell, which underwent a most phenomenal growth under his direction.

Caldwell's "Agricultural Chemical Analysis," published in 1869, was the first work upon this subject in the English language and remained for many years a standard treatise. Another important contribution was Caldwell's account of "The More Notable Events in the Progress of Agricultural Chemistry since 1870,"[1] in which the work of Armsby, Atwater, Babcock, Chittenden, Collier, Hilgard, King, Neale, Osborne, Scovell, Stone, Whitney, Wiley, Woods, and other American investigators is carefully reviewed.

Federal and State Workers

A very important factor in the growth of agricultural chemistry in America during the past fifty years was the development of chemical work in the United States Department of Agriculture, which was established in 1862. Twenty years previous to this date the United States Patent Office began publishing annual reports upon agriculture which contained, among other articles, miscellaneous contributions by L. C. Beck, J. C. Booth, T. G. Clemson, Ebenezer Emmons, C. T. Jackson, J. von Liebig, C. Morfit, J. P. Norton, C. U. Shepard, and other scientists upon the chemistry of soils and fertilizers; the chemical composition of grains, vegetables, and fruits; and the applications of chemistry

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[1] *J. Am. Chem. Soc.*, **14**, 83 (1892).

to various branches of agricultural technology. At about this period several of the states began to establish departments of agricultural chemistry, the first to take steps in this direction being Maryland, whose legislature at the session of 1847–1848 created the office of state agricultural chemist with James Higgins as the first appointee. W. W. Mather (1804–1859), who in his work in 1835 upon the salts of aluminum made the first atomic weight determination in the United States, was agricultural chemist for Ohio from 1850 to 1854.

The first chemist of the United States Department of Agriculture was C. M. Wetherill (1825–1871), who obtained his training under Liebig at Giessen and began work for the Government in 1862. Following him were Henry Erni, Thomas Antisell, and R. T. Brown.

WILLIAM MCMURTRIE.—In 1873 William McMurtrie (1851–1913), President of the AMERICAN CHEMICAL SOCIETY in 1900, was appointed chief chemist of the Department of Agriculture and retained this office until 1878. He then served as agricultural technologist of the Department until 1882, when he accepted the professorship of chemistry at the University of Illinois. In 1888 he accepted a position as consulting chemist of the Royal Baking Powder Company, of which he afterwards became manager and vice president. Numerous reports upon wine production, sumac, beet sugar, textiles, guano, and other subjects indicate the extent of Dr. McMurtrie's interest in agricultural chemistry.

PETER COLLIER.—Peter Collier, a pupil of S. W. Johnson, succeeded McMurtrie as chief chemist of the Department of Agriculture but resigned this position in 1883, afterwards becoming director of the New York Agricultural Experiment Station at Geneva. Dr. Collier is best known for his extensive researches and publications upon sorghum.

HARVEY W. WILEY.—In 1883 H. W. Wiley (1844–), President of the AMERICAN CHEMICAL SOCIETY in 1893 and 1894, was appointed chief chemist of the Department of Agriculture. The Chemistry Division of the Department, when he assumed its direction, was located in two small rooms in the basement of the old agricultural building and had a personnel of only three, which number had expanded at the time of his resignation in 1912 to over five hundred.

The impress which Dr. Wiley gave to the work of the Bureau of Chemistry and to agricultural chemistry generally during the twenty-nine years of his governmental service has been of a lasting character. His series of annual reports upon the sugar beet is one of the best examples of an agricultural chemical survey of a crop. His numerous bulletins upon the composition and technology of human foods are still authoritative after more than a quarter of a century. By his publications upon the adulteration and debasement of foods he secured, after years of strong opposition by powerful interests, the final passage of the federal food and drugs act of 1906, one of the finest pieces of constructive legislation ever enacted.

Another important event in the history of agricultural chemistry in America during the past fifty years was the founding of the Association of Official Agricultural Chemists, and in the work of that society Dr. Wiley has played a conspicuous part. In 1880 J. T. Henderson, commissioner of agriculture for Georgia, issued an invitation for prominent American agricultural chemists to meet in Washington, on July 28, at the Department of Agriculture, for the purpose of securing greater uniformity in the methods of analyzing commercial fertilizers. A second meeting, under the chairmanship of C. A. Goessmann, was held at Boston on August 27, 1880, as a subsection of the American Association for the Advancement of Science, and a third meeting convened at Cincinnati on August 18, 1881. In these early meetings trade chemists and official chemists took equal part, but it soon became evident that coöperation between these discordant elements was impossible and no further meetings of this preliminary organization were held. Finally, at the meeting of the American Association for the Advancement of Science at Philadelphia in 1884, the present Association of Official Agricultural Chemists was organized on September 9 under the initiative of H. W. Wiley, H. C. White, E. H. Jenkins, J. A. Myers (1853–1901), C. W. Dabney, and others, with S. W. Johnson as the first president. Dr. Wiley was elected the second president in 1886 and G. C. Caldwell the seventh president in 1891. These three presidents of the Association of Official Agricultural Chemists have also been Presidents of the AMERICAN CHEMICAL SOCIETY. Dr. Wiley has the unique distinction of having attended all the forty-one annual meetings of the Association of Official Agricultural Chemists. He was secretary of the association from 1890 until 1913 and honorary president from 1913 until the present time.

The work of the Association of Official Agricultural Chemists has expanded from the unification of methods for analyzing fertilizers, which was the sole purpose of the first meeting, to the chemical examination of all classes of agricultural products, and its official methods of analysis are regarded as authoritative in all parts of the world. By his work in this association and by his three-volume "Principles and Practices of Agricultural Analysis," Dr. Wiley has rendered this branch of agricultural chemistry most valuable service.

STEPHEN M. BABCOCK.—Another distinguished octogenarian and connecting link between the old order and the new in American agricultural chemistry is S. M. Babcock (1843–). After graduating from Tufts College in 1866, he taught chemistry for several years and then took a postgraduate course at Göttingen, where he received his doctor's degree in 1879. He was chemist of the New York Agricultural Experiment Station at Geneva from 1882 to 1888, and then accepted a call to the University of Wisconsin, where he filled the dual position of professor of agricultural chemistry and chief chemist of the Agricultural Experiment Station until his retirement in 1913 as professor emeritus. Babcock is distinguished for his researches in dairy chemistry. His invention of the famous Babcock test for determining fat in milk is one of the best examples of the practical usefulness of chemistry to agriculture. The simplicity of the test placed it within the reach of every farmer and it sprang immediately into universal use. It won grand prizes at both the Paris and St. Louis Expositions. Babcock's invention, from the effect which it had in improving dairy herds, in securing the payment for milk and cream upon a fat percentage basis, in controlling the processes of manufacturing dairy products, and in regulating the purity of municipal milk supplies, has been of inestimable value to the American people, although he himself, by generously dedicating his process to the public, has had no share in the vast financial benefits which others have acquired.

By his work upon the fermentation of cheese and in plant physiology Professor Babcock has made other important contributions to agricultural chemistry. He took a prominent part in the early meetings of the Association of Official Agricultural Chemists and was president of that organization in 1893.

WILBUR O. ATWATER.—A special department of agricultural chemistry in which American scientists have won great distinction is that of human and animal nutrition. The chemist who laid the foundation of exact investigations in this field in the United States was W. O. Atwater (1844–1907), whose work upon human nutrition is described in Chapter X by Graham Lusk. Atwater during his studies abroad familiarized himself with the work of European agricultural experiment stations and after his return to the United States immediately lent his support to the efforts of S. W. Johnson to establish an agricultural experiment station in

Connecticut after European models. The first result of this movement, as already stated, was the establishment of the first state agricultural experiment station in the United States at Middletown on July 2, 1875, with Atwater as director.

Although the Middletown experiment station was discontinued after two years, Atwater continued to occupy himself with agricultural chemical investigations. He organized an extensive series of field experiments with fertilizers and, together with his assistant, the late C. D. Woods (1856–1925), demonstrated that free atmospheric nitrogen is assimilated by leguminous crops. This work, which was reported at meetings of the American Association for the Advancement of Science in 1881 and 1882, is regarded by many as the first convincing proof of this important function of the legumes.

Atwater continued to keep in closest touch with the experiment station movement and became the chief advocate of a general law for the federal support of agricultural investigations in all the different states. His efforts contributed largely to the passage of the famous Hatch Act of 1887, which granted fifteen thousand dollars annually to each state and territory for the maintenance of one or more agricultural experiment stations. Under this provision Connecticut awarded half of the income which it received under the Hatch Act to the previously established experiment station at New Haven, of which S. W. Johnson was director, and half to the establishment of a new experiment station at Storrs, with Atwater as director.

There was a widespread belief at the beginning that the chief purpose of the agricultural experiment stations was the regulatory function of preventing the adulteration of commercial fertilizers. Atwater, however, was strongly opposed to this narrow opinion, as is shown by his declaration in the same year that the Hatch Act was passed: "The future usefulness of the stations will depend upon what they discover of permanent value, and this must come largely from the most abstract and profound research; to forget this will be fatal." As the stations began to take up their more proper experimental functions, the chemical control of fertilizers, feeding stuffs, food products, insecticides, etc., became more and more subordinated to investigational work in crop and animal production. In many states the experiment stations have been entirely relieved of control work by the transference of their former regulatory activities to the state chemist.

In 1888, at the request of Commissioner Coleman, Professor Atwater, without relinquishing his other duties, established the federal Office of Experiment Stations of which he became the first director.

Henry P. Armsby.—A direct outcome of Atwater's calorimetric investigations upon human beings was the development of similar researches upon farm animals by H. P. Armsby (1853–1921) at the Pennsylvania Agricultural Experiment Station. Armsby's prominence as the leading American authority upon the nutrition of farm animals dated from the publication of his "Manual of Cattle Feeding" in 1880, while he was chemist of the Connecticut Agricultural Experiment Station. This work caused the study of animal nutrition, which had hitherto been largely neglected in the United States, to be considered with much greater attention.

With the passage of the Hatch Act in 1887 Armsby became the first director of the Pennsylvania Agricultural Experiment Station, at State College, and retained this position during the next twenty years. In this period he gave an increasing amount of attention to the scientific feeding of farm animals, with the result that in 1898 the United States Department of Agriculture provided means for erecting at State College a special respiration calorimeter, of the Atwater-Rosa type, for studying the food requirements of live stock. The first experiments with the new apparatus were begun in the winter of 1901–1902, and as the work progressed the possibilities which it afforded of accurately determining the energy requirements of farm animals became more and more apparent. With the growing realization of the importance of the work it was finally decided to detach the animal nutrition investigations from the other activities of the Pennsylvania Experiment Station and to organize it as a separate unit. This led in 1907 to the establishment of the Pennsylvania State College Institute of Animal Nutrition of which Armsby was made director following his resignation as head of the Experiment Station.

Armsby's contributions to the science of animal nutrition have been of the greatest value. He devoted many years to a study of the economic need of converting the numerous agricultural wastes that are unsuited for human food into meat and milk. He pointed out the vast losses of energy that are involved in diverting products which are suitable for direct human consumption to the feeding of farm animals. His policy for the conservation of food materials during the World War was based in fact upon the economic adjustment of the supplies of human and animal foods.

Armsby's chief contribution to the science of animal nutrition was his employment of net energy as a basis for measuring the nutritive value of food materials. According to this conception the difference between the gross energy of the food before consumption and that expended and lost in the process of its utilization represents the net energy value of the food for purposes of maintenance and production. Armsby's determinations of the net energy values of the principal American feeding stuffs and his use of these in place of the old digestion coefficients for computing the rations of farm animals form one of the most important contributions to agricultural chemistry which has been made in recent years. Armsby's researches in the field of animal nutrition have been summarized in several books—"Principles of Animal Nutrition," "The Nutrition of Farm Animals," "The Conservation of Food Energy" (published in 1918 with reference to the food situation during the World War), and "The Animal as a Converter of Matter and Energy," which was prepared after Armsby's death by his collaborator, C. R. Moulton, as one of the AMERICAN CHEMICAL SOCIETY Monograph Series.

The work initiated by Armsby has been continued at State College since 1922 by E. B. Forbes, the present director of the Institute of Animal Nutrition, in collaboration with Armsby's former associates, J. A. Fries and W. W. Braman.

Later Developments

The work in American agricultural chemistry which has thus far been described was conducted mostly by men who were born before 1850. These were the chemists who laid the broad foundations of the science as it is being applied to the needs of American agriculture today. But the description of their accomplishments has supplied only the general background of the picture, which is still lacking in many important details. The number of workers in this field who were born since 1850 is so large and the range of their activities so diverse that it will be possible in the remainder of this review to discuss only very briefly a few of the present-day applications of chemistry to American agriculture.

A great difficulty in making a survey of this character is the difference of opinion which prevails respecting the demarcations of agricultural chemistry. The latter, in its generally accepted meaning, may be defined as that branch of chemistry which treats of the chemical composition of soils, crops, and animals, and of the mutual chemical relations of these in so far as they concern the production of the means of human subsistence and welfare. There is no field of applied chemistry which is so broad in its scope or so comprehensive in its bearings as that pertaining to agriculture, including, as it does, not only many branches of chemistry but touching also upon mineralogy, physics, meteorology, plant and animal physiology, mycology, and other correlated sciences.

It is held by many that agricultural chemistry relates solely to the production of raw materials, such as grain, vegetables, fruit, live stock, milk, hides, wool, etc., and not to their utilization. Yet in many cases the manufacture of butter, cheese, vinegar, sirup, sugar, canned goods, etc., from raw materials is performed directly on the place of production and constitutes an integral part of the farm operations. The opinion has also been expressed that human nutrition and the chemical control of human foods lie outside the province of agricultural chemistry. Yet the nutritive needs of the farmer and his family must be considered as essential factors in the successful management of the farm, and the farmer, moreover, cannot ignore the regulatory requirements which govern the sale of his milk and other produce. Agricultural chemistry is, therefore, closely concerned with the utilization and disposition of manufactured products of farm origin, although it is less actively engaged in these phases of the subject than in the production of raw materials.

A compilation of projects of American agricultural experiment stations, prepared in 1923 by E. R. Flint (1864–1926), shows that of the investigations which involve chemistry 188 relate to soils; 150 to fertilizers; 111 to animal nutrition; 73 to insecticides, fungicides, etc.; 57 to dairy products; 49 to plant nutrition; and 45 to various miscellaneous studies of foods, etc. These figures show in a general way the relative stress which is now being placed by American experiment stations upon certain applications of chemistry to agriculture.

SOILS.—In point of utility the investigations of H. J. Wheeler and his co-workers at the Rhode Island Experiment Station upon acid soils are of exceptional importance. The practical value of this work to American agriculture in restoring fertility to barren lands by the addition of lime is incalculable. The study of the causes, effects, and elimination of soil acidity is a question that has engaged a large number of American chemists: William Frear (1860–1922) in Pennsylvania; B. L. Hartwell in Rhode Island; S. D. Conner and H. A. Noyes in Indiana; W. H. MacIntire in Tennessee; D. R. Hoagland in California; Emil Truog in Wisconsin; J. K. Plummer in North Carolina; and F. P. Veitch and E. T. Wherry at the Bureau of Chemistry are only a few of those who have made contributions to this subject. The injurious effects of soluble salts of aluminum, iron, and manganese upon crops which are grown in acid soils has been investigated, among others, by R. W. Ruprecht in Massachusetts; by Emil Truog in Wisconsin; by B. L. Hartwell, F. R. Pember, and P. S. Burgess in Rhode Island; and by S. D. Conner and J. S. Abbott in Indiana. The effect of salts and of heat upon soils and the transformation of nitrogen in soils have been studied by W. P. Kelley in Hawaii and California. T. L. Lyon has made experiments with lysimeters and has investigated the influence of higher plants on bacterial processes in soils.

The causes, effects, and removal of alkalinity in soils have continued to attract the attention of chemists in the western states since the early investigations of E. W. Hilgard. The recent work of P. L. Hibbard in California upon reclaiming alkali soils by leaching with water and gypsum and the studies of alkali and plant food under irrigation and drainage by C. W. Botkin in New Mexico are mentioned in this connection.

The processes of oxidation, reduction, nitrification, denitrification, etc., by which the organic matter of soils is transformed by bacteria and other agencies, have been studied by E. B. Voorhees and J. G. Lipman in New Jersey; by W. A. Withers and by L. G. Willis in North Carolina; by G. S. Fraps in Texas; and many others. The first award of the Nichols Medal by the New York Section of the AMERICAN CHEMICAL SOCIETY was made to E. B. Voorhees for his "Studies in Denitrification."[1] The organic substances which are formed in soils by the decay of plant and animal residues have been extensively investigated by Oswald Schreiner and his collaborators, E. C. Shorey, J. J. Skinner, M. X. Sullivan, H. S. Reed, B. E. Brown, and E. C. Lathrop of the Bureau of Soils. The hypothesis of toxic exudates from the roots of crops, as a cause of unproductiveness in soils, originally proposed by the Bureau of Soils, attracted considerable attention at the time it was announced but has not met with general acceptance. The important work of F. K. Cameron of the Bureau of Soils upon "The Soil Solution" has been noted in Chapter VII upon "Physical Chemistry," by W. D. Bancroft.

WATERS.—In the more or less arid agricultural regions of the country the chemical composition of the water which is used for irrigating land or watering livestock is of considerable importance. The subject has been studied from various angles by E. W. Hilgard, R. H. Loughridge, W. P. Kelley, and C. B. Lipman in California; by R. H. Forbes and W. W. Skinner in Arizona; by

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[1] *J. Am. Chem. Soc*, **24**, 785 (1902).

J. E. Greaves, Robert Stewart, and J. A. Widtsoe in Utah; by W. P. Headden in Colorado; by F. W. Traphagen in Montana; by G. S. Fraps in Texas; and by numerous others.

FERTILIZERS.—Chemical analyses and field tests of fertilizers have engaged the attention of American agricultural experiment stations since the time of their establishment. The agricultural station at State College, Pennsylvania, has a record of field tests beginning with 1882 which are the oldest extensive experiments with fertilizers now in progress in America. The field tests upon fertilizers conducted by William Frear in Pennsylvania; by E. B. Voorhees and J. G. Lipman in New Jersey; by H. J. Wheeler and B. L. Hartwell in Rhode Island; by C. E. Thorne in Ohio; by C. G. Hopkins (1866–1919) in Illinois; by Harry Snyder in Minnesota; by W. C. Stubbs (1843–1924) in Louisiana; and by F. T. Shutt and C. E. Saunders in Canada are mentioned simply as typical examples of the work which has been conducted in this field. A very good summary of fertilizer experimentation in America is contained in "Soil Fertility and Permanent Agriculture" by C. G. Hopkins, distinguished for his work upon the role of phosphorus in crop production and upon the relation of phosphates to permanent fertility. The volume upon "Fertilizers" by E. B. Voorhees is also worthy of mention.

As a consequence of the threatening shortage of fertilizers during the World War much attention was given by American chemists to developing domestic sources of potassium salts and to perfecting methods for nitrogen fixation. The Bureau of Soils and the Nitrogen Fixation Laboratory of the United States Department of Agriculture have taken a prominent part in the improvement of processes for manufacturing concentrated potassic and nitrogenous fertilizers.

A study of the fertilizing value of previously neglected elements is engaging the attention of various American chemists. The relation of sulfur to soil fertility has been investigated by W. E. Tottingham in Wisconsin; by G. A. Olson in Washington; by J. G. Lipman in New Jersey; and others. J. S. McHargue of Kentucky has made valuable studies regarding the effects of manganese upon plant growth.

ANIMAL NUTRITION.—Feeding experiments with farm animals for working, or for the production of meat, milk, etc., have been undertaken at most of the American agricultural experiment stations, with the major interest in New York, Pennsylvania, Illinois, Wisconsin, Missouri, and Minnesota. The results of this work are too compendious for the mention of particular workers. The first compilation upon the composition of American feeding stuffs was made by E. H. Jenkins of Connecticut in 1879. More extensive summaries were made later by W. H. Jordan of New York and J. B. Lindsey of Massachusetts. A very complete "Compilation of Analyses of American Feeding Stuffs" was published by E. H. Jenkins and A. L. Winton as Experiment Station Bulletin No. 11 of the United States Department of Agriculture. Tables of the composition and digestibility of American feeding materials are also contained in the treatise of W. A. Henry and F. B. Morrison of the Wisconsin station upon "Feeds and Feeding."

The subject of mineral metabolism in farm animals has been studied at various agricultural experiment stations. E. B. Forbes at the Ohio station has studied the metabolism of phosphorus and other mineral ingredients in cows and swine. The metabolism of calcium in laying hens has been investigated by G. D. Buckner, J. H. Martin, and A. M. Peter at the Kentucky station. C. R. Moulton, P. F. Trowbridge, and L. D. Haigh have made exhaustive studies in Missouri upon the distribution of ash and phosphorus in the bodies of cattle. The importance of iodine in the diet, with special reference to the prevention of goiter in animals, has been studied by G. E. Smith; by E. B. Hart and Harry Steenbock of Wisconsin; by J. F. McClendon of Minnesota; and many others. A correlation of manganese content with vitamin potency in the organs of animals has been noted by J. F. McHargue at the Kentucky station. In addition to the names mentioned, C. H. Hunt and A. R. Winter of the Ohio station, H. G. Miller of Oregon, and many others have studied the significance of particular mineral constituents in animal nutrition.

The important researches of T. B. Osborne at the Connecticut station upon the chemistry of the vegetable proteins and the work of American chemists upon vitamins and other phases of animal nutrition are fully discussed in Chapter X by Graham Lusk.

DAIRY PRODUCTS.—Great advances have been made in the United States during the past fifty years in the applications of chemistry to dairying and to dairy products. L. L. Van Slyke has investigated the chemistry of cheese-making, the proteins of milk products, and the chemical changes which are produced in the souring and curdling of milk. Results upon the preservation of milk by charging it with carbon dioxide under pressure were published in 1907 by L. L. Van Slyke and A. W. Bosworth. More recently the introduction of commercial processes for the preservation of milk, butter, and ice cream by means of carbon dioxide has led to a general study of the carbonation of dairy products at the Illinois Experiment Station. E. B. Hart, E. H. Farrington, F. W. Woll (1865–1922), and their co-workers at the Wisconsin station have devoted much attention to the chemistry of dairy products. The chemistry of rancidity in butter fat was investigated by C. A. Browne at the Pennsylvania station in 1899 and more recently by G. E. Holm of the United States Bureau of Dairying. E. B. Holland has studied the composition of butter fat and its modification as a result of feeding. The chemistry and physical chemistry of churning is being investigated at the Minnesota station. G. C. Supplee and J. T. Cusick of the Cornell Experiment Station and H. H. Sommer and B. J. Smit of the Wisconsin station have found that the abnormal fishy flavor of butter is due to the decomposition of lecithin into trimethylamine. The yellow pigment of milk fat and its relation to the plant carotins have been exhaustively studied by L. S. Palmer and C. H. Eckles at the Minnesota station. The clarification and pasteurization of milk, the preparation of milk powders and modified milks, methods for improving ice cream, the manufacture of foreign types of cheese, the utilization of whey, the reduction of butter fat losses in churning, and numerous other problems in dairy technology are being actively investigated by American chemists.

Great progress has also been made in the improvement of methods for analyzing dairy products. The apparatus of J. J. Mojonnier for determining fat in dairy products by the modified Röse-Gottlieb method has found extensive use. Other improvements in methods and apparatus for analyzing milk and its products have been made by J. C. Baker, E. B. Hart, Julius Hortvet, G. E. Patrick (1851–1916), G. C. Supplee, L. L. Van Slyke, and W. O. Walker—to mention only a few of many names.

Crops.—In the chemistry of crops American investigators have made contributions in numerous fields. J. P. Norton was one of the earliest to specialize in the chemistry of particular crops and won a prize of fifty guineas eighty years ago from the Scotch Highland Society for his essay upon "The Oat." Of the more recent chemical studies upon cereals may be mentioned the work of Clifford Richardson at the Bureau of Chemistry, of Harry Snyder in Minnesota, and of E. F. Ladd (1859–1925) in North Dakota upon wheat; of C. G. Hopkins in Illinois upon corn; and of B. B. Ross, C. A. Browne, C. C. McDonnell, and others upon rice. Investigations upon the chemistry of apples and other fruits have been made by W. B. Alwood, W. D. Bigelow, F. C. Blanck, C. A. Browne, E. M. Chace, A. W. Christie, H. C. Gore, and many others. C. H. Jones has studied the chemistry of the maple tree and maple sap.

Chemical investigations upon the sugar cane and its products in Louisiana were initiated by Avequin in 1840, but were first followed up intensively with the establishment by W. C. Stubbs (1843–1924) of the Louisiana Sugar Experiment Station in 1885. Among those who have conducted agricultural chemical work at this station may be mentioned R. E. Blouin, J. F. Brewster, C. A. Browne, C. E. Coates, W. E. Cross, J. M. Schneller, P. A. Yoder, and F. W. Zerban. Similar studies have been conducted in Hawaii by H. P. Agee, Noel Deerr, C. F. Eckart, Walter Maxwell, and R. S. Norris. Investigations upon sugar crops and sugars have also been conducted at the United States Bureau of Chemistry by D. H. Brauns, C. A. Browne, A. H. Bryan (1874–1920), C. A. Crampton, (1858–1915), H. C. Gore, C. S. Hudson, H. S. Paine, S. F. Sherwood, G. L. Spencer (1858–1925), C. F. Walton, Jr., H. W. Wiley, and many others. A study of the Jerusalem artichoke as a source of levulose has been undertaken at the United States Bureau of Standards by F. J. Bates, R. F. Jackson, M. J. Profitt, and C. J. Silsbee.

The chemistry of the cotton plant has been investigated, or reported upon, by J. B. McBryde and W. H. Beal; by F. B. Power and V. K. Chesnut; by H. C. White; by W. A. Withers (1864–1924); and by many others. The chemistry of tobacco growing and curing has been studied by William Frear in Pennsylvania and E. H. Jenkins in Connecticut. Of the more special studies in phytochemistry may be mentioned the work of F. B. Power and V. K. Chesnut upon the odorous principles of fruits, of G. S. Jamieson upon the vegetable oils, of E. K. Nelson upon the vegetable acids, and of R. J. Anderson upon the pigments of the grape. The chemistry of the pectins has been studied by E. K. Nelson, W. H. Dore, C. P. Wilson, L. W. Tarr, and others. The studies of L. S. Palmer and his co-workers upon the caritinoids and related pigments are included in his exhaustive review of this subject in the AMERICAN CHEMICAL SOCIETY Monograph Series. The chemical composition of American honeys, as influenced by different floral nectars, has been investigated by C. A. Browne, A. H. Bryan (1874–1920), and others. The modification of the composition of wheat and other cereals by fertilization has been studied by J. A. LeClerc and Jehiel Davidson.

INSECTICIDES AND FUNGICIDES.—The prevention of the enormous losses to agriculture from insect pests and fungous diseases is a subject in which American chemists have taken a leading part. Paris green, which was introduced shortly before 1870 to combat the potato bug, was the first important chemical to be used for destroying insects, but is now surpassed as a general insecticide by other arsenical preparations. Lead arsenate, first employed in Massachusetts in 1892 to destroy the gypsy moth, is probably the most generally used arsenical insecticide. Calcium arsenate, which exceeds other insecticides in quantity production, is mostly employed for combating the cotton boll weevil, being first used for this purpose in 1918. The chemistry of the various arsenicals has been investigated by J. K. Haywood, C. C. McDonnell, C. M. Smith, R. H. Robinson, H. V. Tartar, and others. For destroying insects in grain, carbon disulfide is the most extensively used fumigant but has the serious objection of inflammability. Hydrocyanic acid, introduced as a fumigant by the United States Department of Agriculture in 1886, is highly effective but dangerous. Efforts to develop less hazardous fumigants have been made by J. E. Neifert, F. C. Cook (1877–1923), R. C. Roark, and others. Chloropicrin and ethyl acetate have shown some promise in this connection. The perfection of various petroleum emulsions for combating sucking insects and the development of cheap effective substitutes for nicotine, pyrethrum, and other expensive insecticides are receiving considerable attention. The use of organic substances for attracting or repelling insects is also being investigated. Amyl acetate has been employed in poisoned baits as an attractant for grasshoppers and geraniol has been proposed as a means of luring Japanese beetles into traps. Trimethylamine, discovered by F. B. Power and V. K. Chesnut among the odorous constituents of the cotton plant, has been found to attract the boll weevil.

Bordeaux mixture, discovered by Millardet of France in 1880, is the most extensively used fungicide in the United States. The chemistry of its composition and action has been recently investigated by F. C. Cook. Lime-sulfur solution is another fungicide which has been widely studied by American chemists, more especially by R. W. Thatcher, J. K. Haywood, L. L. Van Slyke, C. C. Hedges, and A. W. Bosworth. The effectiveness of copper carbonate and other chemicals in preventing smuts of grain is being investigated at various experiment stations.

The Louisiana enactment of 1890 which regulated the purity of Paris green was the first state insecticide law. At present twenty-eight states have laws relating to insecticides and fungicides.

E. D. Sanderson, director first of the New Hampshire and later of the West Virginia Experiment Station, and J. K. Haywood of the Bureau of Chemistry were largely instrumental in securing the passage of the federal law of 1910, which has had a most beneficial effect upon the improvement of insecticides and fungicides in the United States.

FOOD TECHNOLOGY.—Much attention is being given in the United States to the chemistry and technology of foods and other agricultural products by industries, coöperative research laboratories, experiment stations, and various institutions of learning. The Louisiana Sugar Experiment Station, the Minnesota State Testing Mill for examining wheat, the American Institute of Baking, the National Canners Association, the Meat Packers Institute, the Mellon Institute, the Boyce-Thompson Institute, the research laboratories of the California Fruit Growers Exchange, the fruit and vegetable laboratory of the University of California, the Tanners' Research Laboratory of the University of Cincinnati, the research laboratory of the Glass Container Association, the New York Sugar Trade Laboratory, and the various fruit, vegetable, cereal, meat, dairy, and other special laboratories of the United States Department of Agriculture are a few examples of institutions which are conducting chemical and technological studies upon the numerous special products of agricultural origin. Many investigations of this character have also been performed by private enterprise. The researches of Arno Behr (1846–1921) upon the utilization of corn products, and of David Wesson upon the utilization of cottonseed products as food are illustrations of industrial chemical work which has been of the greatest benefit to American agriculture.

FOOD CONTROL.—The control of the purity of milk, butter, cheese, grain, and numerous other agricultural products engages the attention of thousands of chemists in the various municipal, state, and federal laboratories of the United States. Following the passage of different state laws and of the federal food and drugs act of 1906, there has been a great improvement in the character of the food products which are now sold in the United States. Among the chemists who have taken an active part in improving the purity of the Nation's food supplies may be mentioned J. S. Abbott, C. L. Alsberg, E. M. Bailey, R. W. Balcom, H. E. Barnard, W. D. Bigelow, F. C. Blanck, L. P. Brown, R. E. Doolittle (1874–1926), P. B. Dunbar, F. L. Dunlap, R. L. Emerson, G. G. Frary, William Frear, W. S. Frisbie, Elton Fulmer (1864–1916), W. C. Geagley, W. F. Hand, B. R. Hart, R. W. Hilts

(1879–1924), Julius Hortvet, C. D. Howard, M. E. Jaffa, E. H. Jenkins, E. F. Ladd (1859–1925), A. E. Leach (1864–1917), H. M. Loomis, H. C. Lythgoe, I. L. Miller, A. S. Mitchell, A. E. Paul, I. K. Phelps, W. W. Randall, Clifford Richardson, R. W. Redfield, R. E. Rose, M. A. Scovell (1855–1912), A. F. Seeker (1878–1919), W. W. Skinner, J. P. Street, L. M. Tolman, H. A. Weber (1845–1914), H. W. Wiley, and A. L. Winton—to name only a few of the prominent workers in this field.

Chemistry in the Direction of Agricultural Research

Limitations of space prevent the enumeration of many other important subjects in which chemistry is being applied to agriculture. The recent work, "Chemistry in Agriculture," edited by J. S. Chamberlain for the Chemical Foundation, contains sixteen chapters by various specialists upon certain applications of chemistry to American agriculture. The recent bequest of Mrs. Herman Frasch for research in agricultural chemistry is an evidence of the growing realization of the value of work in this field.

Perhaps the best evidence of the importance of chemistry to agriculture is the prominent part which chemists have taken in directing agricultural research. The following table gives a list of chemists who have been directors or acting directors of American agricultural experiment stations.

Chemists Who Have Been Directors or Acting Directors of American Agricultural Experiment Stations

NAME	STATION	PERIOD OF OFFICE
H. P. Agee	Hawaii, Sugar Planters	1913–
H. P. Armsby	Pennsylvania	1887–1907
H. P. Armsby	Pennsylvania Institute of Animal Nutrition	1907–1921
W. O. Atwater	Connecticut, Middletown	1875–1877
W. O. Atwater	Connecticut, Storrs	1887–1901
J. M. Bartlett*	Maine	Dec., 1920–Apr., 1921
H. B. Battle	North Carolina	1887–1897
R. E. Blouin	Hawaii, Sugar Planters	1900–1901
G. C. Caldwell	New York, Cornell	1879–1888
G. W. Carver	Alabama, Tuskegee	1900–
P. Collier	New York, Geneva	1887–1895
G. H. Cook	New Jersey	1880–1889
W. W. Cooke	Vermont	1887–1893
J. T. Crawley	Porto Rico, Sugar Producers	1910–1914
C. W. Dabney, Jr.	North Carolina	1880–1887
C. W. Dabney, Jr.	Tennessee	1887–1890
C. T. Dowell	Oklahoma	1921–
C. F. Eckart	Hawaii, Sugar Planters	1901–1913
John Fields	Oklahoma	1899–1906
E. B. Forbes	Pennsylvania Institute of Animal Nutrition	1922–
R. H. Forbes	Arizona	1899–1918
C. P. Fox	Idaho	1894–1896

Chemists Who Have Been Directors or Acting Directors of American Agricultural Experiment Stations (Concluded)

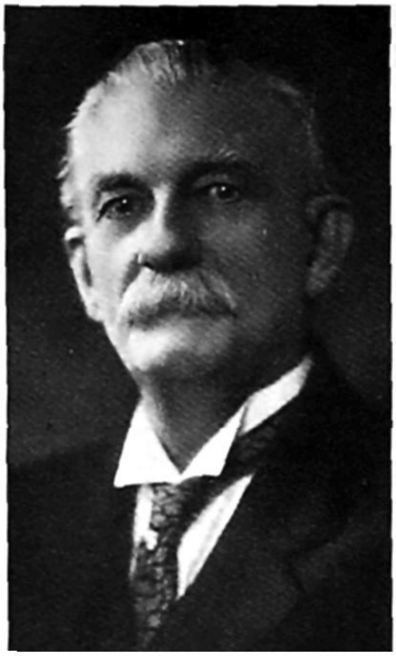
NAME	STATION	PERIOD OF OFFICE
C. A. Goessmann	Massachusetts	1882–1895
Arthur Goss	Indiana	1903–1917
H. H. Harrington	Texas	1906–1911
F. S. Harris	Utah	1917–1921
B. L. Hartwell	Rhode Island	1912–
E. W. Hilgard	California	1874–1908
J. L. Hills	Vermont	1893–
H. A. Huston	Indiana	1902–1903
W. L. Hutchinson	Mississippi	1898–1910
E. H. Jenkins	Connecticut	1900–1923
S. W. Johnson	Connecticut, New Haven	1877–1899
W. H. Jordan	Maine	1885–1896
W H. Jordan	New York, Geneva	1896–1921
J. H. Kastle	Kentucky	1912–1916
B. W. Kilgore	North Carolina	1901–1907; 1912–1925
H. G. Knight	Wyoming	1910–1918
H. G. Knight	Oklahoma	1918–1921
H. G. Knight	West Virginia	1922–
A. R. Ledoux	North Carolina	1877–1880
J. G. Lipman	New Jersey	1911–
T. L. Lyon*	Nebraska	1899–1905
Walter Maxwell	Hawaii, Sugar Planters	1895–1900
J. M. McBryde	South Carolina	1887–1890
J. M. McBryde	Virginia	1892–1904
C. A. Mooers	Tennessee	1923–
F. B. Morrison*	Wisconsin	1924–1925 (5 mos.), 1926
F. W. Morse*	New Hampshire	1912–1913
F. W. Morse*	Massachusetts	1918–1920
J. A. Myers	West Virginia	1887–1897
A. T. Neale	Delaware	1888–1906
H. H. Nicholson	Nebraska	1890–1893
H. J. Patterson	Maryland	1898–
A. M. Peter	Kentucky	Aug., Oct , 1912;* Jan.–Feb., 1915;* 1916–1917
J. P. Schweitzer	Missouri	1888–
M. A. Scovell	Kentucky	1885–1912
J. H. Shepard	South Dakota	1895–1900
Longfield Smith	Virgin Islands	1918–1921
H. E. Stockbridge	Indiana	1889–1890
H. E. Stockbridge	North Dakota	1890–1893
W. C. Stubbs	Louisiana	1885–1905
R W. Thatcher	Washington	1907–1913
R W. Thatcher	Minnesota	1917–1921
R. W. Thatcher	New York, Geneva	1921–
R. W. Thatcher	New York, Cornell	1923–
P. F. Trowbridge	North Dakota	1918–
L. L. Van Slyke*	New York, Geneva	1895–1896
E. B. Voorhees	New Jersey	1893–1911
H. J. Wheeler	Rhode Island	1900–1912
J. A Widtsoe	Utah	1900–1905
J. T. Willard	Kansas	1900–1906
W A. Withers*	North Carolina	1897–1899
C. D. Woods	Maine	1896–1920
P. A. Yoder	Utah	1905–1907

* Acting director

Conclusion

The impetus which the chemists of America gave to agricultural research a half-century ago has been strong and extensive. Beginning with the fundamental problems of soils and fertilizers the movement extended to the complex fields of plant and animal life until now there is not a single department in the whole province of agriculture that is not permeated with the outlook and influences of chemistry. It was fortunate that the foundations of modern agricultural research were laid by chemists, for they imparted to it a definiteness of method and purpose which otherwise would not have been acquired. But while the elements and the processes which govern their combination form the basis for the existence of soils and crops and animals, the aims of agriculture are not so distinctively chemical as was once supposed. With the growing realization of this, the demarcation of chemistry as a separate branch of agricultural research is now much less evident than was the case twenty or more years ago. Chemistry in its relationship to agriculture has changed from an independent to a coöperative science, and it is in the borderland where it and the other sciences meet that the agricultural scientists of the future will find the greatest opportunities for service and accomplishment.

It may be said in conclusion that as the density of population in the United States increases, greater attention must be given to more intensive methods of agriculture. There must be a greater avoidance of waste, a higher yield of crops, a more economical feeding of animals, and a better utilization of raw materials. In all of these lines of advancement chemistry may be expected to play a role of increasing importance.



Sarony

ABRAM A. BRENEMAN
(1847-)
Editor, *Journal of the American Chemical Society* 1884–1893

Alman & Co.

EDWARD HART
(1854-)
Editor, *Journal of the American Chemical Society* 1893–1902

Marshall

ARTHUR B. LAMB
(1880-)
Editor, *Journal of the American Chemical Society* 1917–

AUSTIN M. PATTERSON
(1876-)
Editor, *Chemical Abstracts* 1909–1914

A. A. Breneman attended the Priestley Centennial in 1874.

CHAPTER XII

INDUSTRIAL CHEMISTRY[1]

BY CHARLES E. MUNROE

Introduction

Anniversary celebrations offer a fitting occasion for reviews in which either to beat the drum and scatter compliments, or, perhaps more wisely, to take account of stock for future guidance. A considerable feature of the celebration of the Priestley anniversary in 1874, almost two years before the founding of the AMERICAN CHEMICAL SOCIETY, was the three addresses, respectively, by T. Sterry Hunt on "A Century's Progress in Chemical Theory;" by J. Lawrence Smith on "The Century's Progress in Industrial Chemistry;" and by Benjamin Silliman, Jr., on "American Contributions to Chemistry;" the first, philosophical in treatment; the second, historical with a slightly statistical tone; and the third, bibliographical with much delightful biographical matter intercalated. Together they formed a datum mark for this SOCIETY.

The influence of these men was marked, as is evident by an inspection of the record of the celebration of our Twenty-fifth Anniversary, and especially the "Report of the Census Committee," which consisted of Charles Baskerville, chairman, Louis Kahlenberg, Charles E. Munroe, William A. Noyes, and Edgar F. Smith. This report reviewed the state of preparedness of this country in the field of chemistry, and supplied a mass of useful information and data of permanent value in historical comparisons. Dr. Baskerville rendered yeoman's service in producing such a report under somewhat unfavorable circumstances.

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[1] This chapter was to have been prepared by W A Hamor, assistant director of the Mellon Institute of Industrial Research, University of Pittsburgh, but after having collected his data and partially outlined his plan of treatment he became physically disabled. He most generously turned over all his material to me for use I am also indebted to W. M Steuart, director of the Census, to C A Browne, chief of the Bureau of Chemistry, and to many members of the AMERICAN CHEMICAL SOCIETY, who, either directly or through Dr. Browne, have sent me valuable information and memoranda To all of these I express my appreciation, with the regret that I have been forced to leave unused so much of the material that was placed at my disposal.—C E. M

The report will be found to deal largely with education, though the section on Industrial or Technical Chemistry treats principally of the condition or status of the chemist. The subject of the education of technical chemists was omitted because it had been so fully treated by William McMurtrie in his presidential address in 1900. Statistics of the industry did not appear: first, because reliable ones were then so few; and, second, because the first systematic survey of "Chemicals and Allied Products" was then being made, and its "finals" had not been reduced and authenticated. The results appeared later as Bulletin 210 of the twelfth census of the United States by Charles E. Munroe and Thomas M. Chatard, accompanied with an appendix by Story B. Ladd, entitled "Digest of United States Patents Relating to the Chemical Industries (Products and Processes)." This latter was intended to cover every United States patent relative to the industries treated from the founding of the United States Patent Office up to 1900, but, though this digest covers 306 quarto pages in small pica type, the crowded condition of the Patent Office rendered it uncertain that we had "pulled" every patent, while other circumstances prevented a résumé of apparatus patents.

Subsequent bulletins, not only on "Chemicals and Allied Products," but on "Precious Metals Recovered by Cyanide Process," "Petroleum Refining," "By-product Coke," "Salt," and "Gas," were issued, and résumés were prepared for them which were substantially complete because the Patent Office had caught up in its classification, and because it was found possible to abstract apparatus and analogous patents. Emphasis has been placed here on patents because no complete picture of progress in an art or industry can well be formed without a knowledge of the progress of invention in that art or industry and this is chiefly recorded in patents.

Originally the United States Census of Manufactures was taken every decade; beginning with 1905, every fifth year; and beginning with 1919, every second year. It is hoped that this country may soon make an annual accounting, because such statistics, properly compiled and presented, not only promote industry, foster commerce, inform the financier and the legislator, guide the historian and interest many, but they are essential to the permanence of the Nation. When forced by the exigencies of the World War to ascertain our degree of preparedness and the extent of our resources, those statistics then collected, though not complete, were invaluable.

The census is given prominence in this introduction because we must now go to its records and to those of the Tariff Commission, the Bureau of Foreign and Domestic Commerce, the Geological Survey, and the Bureau of Mines for the quantities and values of the chemical industries through which to gauge and evaluate the progress of any one of them. This matter is germane to our title in that the first effort of the census to collect statistics on Chemicals and Allied Products was made in 1880, while all the other agencies enumerated here have been created during the last fifty years. Furthermore, there is not one of these agencies that has not relied upon the technical chemist for aid and advice. A notable example of the fundamental importance of such statistical inquiries is found in "A Census of Artificial Dyestuffs Used in the United States," by Thomas H. Norton,[1] which was the initial step in releasing us from the forced payment of tribute to a dominant foreign power. Many may recall the protests against the publication of this record, compiled from our Nation's archives, and that certain, most critical, data were suppressed. It is hoped that never again shall vital statistics such as these, entered on the national records, be concealed from our manufacturers, our consumers, or any party in interest.

There were few, if any, men in 1874 so well qualified by training and experience to review the century's progress in industrial chemistry as Dr. J. Lawrence Smith. At twenty-one years of age he had already won his C.E. degree from the University of Virginia and his M.D. degree from the South Carolina Medical School and had had an intervening year of experience in railroad construction. Following the attainment of his medical degree he spent three years in study with Pelouze, Orfila, Dumas, Liebig, Elie de Beaumont, and with eminent physicists, physiologists, and mathematicians of Europe. He became state assayer of South Carolina; he served several years as consultant to the Sultan of Turkey, developing the resources of the Ottoman Empire; he was president and general manager of the Louisville Gas Light Company; with Dr. E. R. Squibb he engaged in the commercial manufacture of analytical reagents and fine chemicals. He was United States commissioner to the Paris Exposition in 1867 and wrote an extensive report on its chemical exhibits, and also one on petroleum which was published in Germany. Yet in his introduction to his Northumberland address Dr. Smith questions the scope of his subject and found difficulty in delimiting it since chemistry reached so far into

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[1] *J. Ind. Eng. Chem.*, **8**, 1039–48 (1916).

the industries. The topic as now viewed goes beyond chemical manufactures and includes the applications of chemistry that affect industry. Hence, the multitude of subtopics can be dealt with only in outline.

To give an idea of the magnitude of the chemical industry of that time Dr. Smith records that "In France alone, the annual value of chemical products is over $250,000,000." The returns for the United States census of 1923 give $708,372,249 for the substances it classes as "Chemical Products." In analyzing its returns for 1909 I found that the value of those substances treated in chemical technologies even then amounted to $4,859,964,000, and it is unquestionably many-fold that amount now.

Gases—Normal, Compressed, and Liquefied

Turning now to the historic gases of Priestley's time, Dr. Smith enumerates eleven different methods of isolating oxygen, refers to the recognition of ozone by Schönbein and, speaking of the, as yet, limited applications of oxygen in the arts, notes that a 500-pound ingot of platinum and iridium, for use in making the standard meters for the United States and other governments, had recently been produced by means of the compound blowpipe, using oxygen in conjunction with hydrogen or hydrocarbons. He expresses the conviction "that the day is not far distant when Priestley's name will not only be connected with the discovery of the corner-stone of modern chemistry, but will also be associated with one of the most useful agents in the chemical arts." With what satisfaction would Dr. Smith learn that in 1923 the United States produced commercially 379,780 thousand-cubic feet of oxygen by the electrolysis of water (his eleventh method) and 2,057,526 thousand-cubic feet from the liquefaction of air, the total having a value of $23,382,236; that oxygen was widely used in therapeutics and industries; that the compound blowpipe was a part of the equipment of most machine shops for use in cutting and welding metals, and that, following Cottrell's suggestion, we now contemplate its use in the blast-furnace and other metallurgical operations.

Compressed and liquefied gases appeared for the first time as a distinct category in the census of 1899 and it included not only oxygen but chlorine also, with SO_2, CO_2, N_2O, NH_3, and others. The oxygen then reported was largely used in the calcium light, which is now displaced by electric lamps. Scheele's gas or chlorine was then principally used in bleaching and disinfection, but the remarkable application of it to water purification and to the chlorination of compounds on a large commercial scale are developments of the last half-century, the chlorine now being largely isolated from chlorides by electrolysis, a process not enumerated by Dr. Smith, and one which has supplanted the chemical processes described by him. The pioneer work in this field in the United States was done by Ernest A. Le Sueur, starting first with Charles N. Waite in 1887 at Newton, Massachussetts, and erecting in 1892 a plant at Rumford Falls, Maine, where caustic soda and bleaching powder were produced.[1] The Dow Chemical Company began producing bleaching powder from electrolytic chlorine in 1898, and many other manufacturers, using a variety of cells, followed. The manufacture of poison gas by the aid of chlorine gave a great impetus to its production and a multitude of uses were developed for it. It is estimated that, in 1925, the yearly capacity of all commercial plants in the United States and Canada was 185,000 tons, to which may be added the idle plant at Edgewood Arsenal, Maryland, with a capacity of 36,500 tons. It is figured that about 65 per cent of the output is consumed in the paper industry, 22 in the textile industries, 10 in sanitation, and the remaining 3 per cent in all other uses.[2]

Of the chlorine produced in 1925, 46,000 tons were liquefied. Liquefied chlorine is shipped in steel cylinders of 10, 20, 100, 150, and 2000 pounds capacity, or steel tank cars, the single-unit ones having a capacity of 15 tons and the multi-unit ones carrying 15 one-ton tanks. There are over 300 steel tank cars and 80,000 steel cylinders in use or available.

To the compressed and liquefied gases above enumerated as entering commerce in the United States may now be added acetylene and other hydrocarbons and hydrogen cyanide, the total value for this category reaching, in 1923, to $54,401,591, the quantity of chlorine attaining 125 million pounds. Recalling our indebtedness to Priestley for carbonated beverages,[3] which in our day have been greatly improved by A. P. Hallock and C. A. Catlin, we note the value for carbon dioxide in 1923 nearly approached $5,000,000, though in 1919 this value was surpassed by $1,500,000. One queries whether, following the outburst of that critical year, there is a falling off in the consumption of soft drinks.

[1] Parsons, C. L , "The Le Sueur Process for the Electrolytic Production of Sodium Hydroxide and Chlorine," *J Am Chem Soc* , **20**, 868–77 (1898).

[2] Pritchard, D A , "Economics of the Chlorine Industry," *Chem Met Eng* , **33**, 350–53 (1926).

[3] Friend, J. Newton, *Chem. Ind* , **45**, 145 (February 26, 1926).

Chemical Substances Produced by Electricity

Another category first appearing in the census of 1899 was "Chemical Substances Produced by the Aid of Electricity," in which sodium, caustic soda and hypochlorites, chlorates, lead oxides, graphite, calcium carbide, carborundum, carbon disulfide, phosphorus and phosphates, were then reported as entering commerce from this source, the total value of these products being given as $2,045,535. It will be noted that aluminum and many of the other metals, and alloys produced by electrothermic methods were not included in the above list. In this connection we may recall the names of Hamilton Y. Castner, J. D. Darling, E. A. Le Sueur, Pedro G. Salom, E. G. Acheson, T. L. Willson, F. A. J. Fitzgerald, and Edward R. Taylor among the pioneers in the development of these new industries. Darling's process for isolating sodium from sodium nitrate, while producing nitric acid, was in operation at the works of Harrison Bros. & Co., Philadelphia, and it was reported that, in December, 1902, the amount of sodium on hand had become so great the city authorities, fearing accidents, compelled the operation of the process to cease. Of the many chemical works which I have visited and of the operations which I have viewed none has given me the sensation with which I witnessed at Taylor's plant, in Torrey, New York, the large-scale continuous production of a low-boiling point, easily ignitable, endothermous substance, such as carbon disulfide, in a large stack furnace in which the melting of the sulfur and its combination with the carbon was effected by electric arcing. It was a most daring development and one little to be expected from a man of Taylor's appearance and bearing. This development came at an opportune time, for though there was use for it as a solvent in many arts, as an efficient insecticide, and as a parent substance in the manufacture of thiocyanides, carbon tetrachloride, sulfocarbonates and other sulfur-containing substances, the great viscose industry, in which carbon disulfide is used to form the cellulose xanthate, was forging to the front. Of special interest among the industries with which I was associated was that operated under Salom's patents wherein native galenite was reduced to metallic lead, this spongy lead then being used as such in the grids of storage batteries, or oxidized to litharge, minium, or peroxide as desired. One of my prized exhibits was a mass of galenite crystals reduced by this process to sponge lead, the mass still retaining the dominant and all the modifying planes of the original crystals. The rate of growth of the industries embraced in this category is shown in that the value of the products returned at the census of 1923 was above $107,000,000, making an increase of over $105,000,000 in 14 years. It is observed that at the 1923 census hydrogen, bromine, ferro-alloys, halogen derivatives, rare metals and alloys, together with other metals and miscellaneous compounds, were added to the list of products reported.

Sulfuric Acid

In dealing with this topic Dr. Smith recalls that pyrites was adopted in England as a source of sulfur because of the shortsighted policy of the King of Naples in granting a monopoly of the Sicilian sulfur and that the use of pyrites spread to other countries, but that the use of sulfur would be resumed when better transportation facilities gave access to our sulfur deposits. The existence of sulfur in Calcasieu Parish, Louisiana, has been long known and some sulfur was secured from the deposit by the Confederates during the Civil War, but though repeated endeavors were made to gain access to this sulfur all failed of economic success because of the nature of the overburden until Herman Frasch devised and developed his ingenious system of annular tubes through which superheated steam might be forced down to the sulfur deposit and the water, primed with molten sulfur, forced to the surface. The effect is seen in the quantities of pyrites used in the chemical industries which fell from some 900,000 tons in 1914 to 471,000 tons in 1923. The use of pyrites will continue as long as they contain values. An achievement of the present half-century is the abating of fume nuisances from smelting operations, such as at Ducktown and Anaconda, through the conversion of the fume contents into useful products, such as sulfuric acid, and in this F. G. Cottrell's precipitator has been an important factor. In 1923, 384,489 tons of 60° Bé. acid were recovered from zinc ores, and 401,300 from copper ores.

Dr. Smith also made the following interesting forecast, "Döbereiner's suggestion of making sulfuric acid in very much smaller apparatus than that now used (by the agency of sulfurous acid, air and spongy platinum) has been tried and worked successfully on a small scale, and its extended success belongs to the future of chemistry." The records show that in the United States in 1923 sulfuric acid (50° Bé. basis) was made by contact processes to the extent of 1,812,341 tons and 4,743,176 tons by chamber processes. Of course the contact-process acid was produced in the higher concentrations known as oleum.

The contact process for the production of sulfuric acid is now a firmly established and thoroughly practicable process but enormous amounts of money and much effort, exerted by many able chemists, have been required to reduce Döbereiner's ingenious idea to practice, even after it has been successfully demonstrated in the laboratory. Among those contributing to this success is J. B. F. Herreshoff, who also devised a very satisfactory and much-used pyrites burner. The developments in chamber processes during the last forty years have recently been admirably set forth by P. C. Hoffman.[1]

Nitric and Mixed Acids

While nitric acid has been used in the manufacture of nitrates, such as those of silver, mercury, lead, and other metals, and in assaying and analytical operations through centuries, it assumed no great commercial importance until its use in nitrating organic substances in the dye and explosives industries began about the middle of the last century. Even in 1899 the quantity produced as compared with sulfuric, or even hydrochloric, acid was relatively small, so that at the census of 1900 but 15,487 short tons (of all grades) were reported. In 1923 this had risen to 113,116 tons. Nitric acid was, and largely is, made by the reaction of sulfuric acid and sodium nitrate. A marked improvement in this process occurred about 1898 with the introduction of the condenser, invented by Edward Hart. More revolutionary methods adopted later were electrical processes for the direct production of nitric acid from atmospheric nitrogen and oxygen, or indirect conversion into nitric acid through cyanamide. The most practicable method appears to be to form ammonia from atmospheric nitrogen and water-gas hydrogen, and then to oxidize this ammonia to nitric acid. This latter method is now established in this country.

It has been found that nitration may be most smoothly and efficiently carried on, to produce either nitric esters or nitro-substitution compounds, by using accurately proportioned mixtures of sulfuric acid with nitric acid, both being of the proper strength. This material in the market is styled "mixed acids." In the census of 1900 the production of mixed acids in 1899 is reported as 21,185 tons. The amount recorded for 1923 was 156,467 tons, of which 102,000 tons were produced by the explosives industry.

But little of the sulfuric acid of mixed acids is expended in nitration and not all of the nitric acid. Hence large quantities

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[1] "Progress in Sulfuric Acid Manufacture," *Chem. Met Eng.*, 33, 406–8 (1926)

of spent acids result from the process. These spent acids have become diluted by the water produced in the reaction and contain dissolved nitrogen oxides resulting from oxidation that runs on concurrently with nitration. Of course they are too valuable to waste, while their disposal as waste would be well-nigh impossible. Practice has varied from time to time as to the methods of recovery of spent acids. They have been treated by steam in towers to separate the nitric acid (and oxides converted to acid) from the sulfuric acid, the latter being reconcentrated for re-use as such, and the weak recovered nitric being used in the manufacture of ammonium nitrate. G. W. Patterson devised a plan for rebuilding spent acid. With oleum at command, rebuilding is a relatively simple matter and is now much practiced.

Nitrogen Fixation

The synthesis of nitrogen compounds from atmospheric nitrogen together with atmospheric oxygen, or hydrogen from various sources, especially as a by-product from many processes, has become one of the most important of chemical industries. I have previously pointed out the military importance of this industry.[1] Although Bradley and Lovejoy had, prior to 1909, demonstrated the feasibility of nitrogen fixation, little commercial or political interest was manifested in these operations in this country until after the World War broke out, when their significance dawned upon the consciousness of our leaders. Hasty efforts were made to remedy the oversight. Norton's report was widely read. C. L. Parsons and Eysten Berg were sent to Europe to report on developments at first hand, and many firms and persons with special processes, such as that of John E. Bucher, were subsidized to promote development. But, except in price-fixing, and in its strategic effect, our activity was too belated. A beneficent outcome, however, was the establishment of the Fixed Nitrogen Research Laboratory, where the economics of the various processes have been investigated and their suitability for use under the varied conditions arising in this vast country determined. Research work, looking to the further perfecting of processes, has also been actively carried on and to such effect that some eight plants are now in operation and others are building. Nevertheless, we are yet but seventh on the list of producing countries, and our output is still less than 10 per cent of that of Germany. Among those active in these investigations may be

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[1] Munroe, Charles E., "The Nitrogen Question from the Military Standpoint," *Proc U. S. Naval Inst*, **35**, 715–27 (1909); Smithsonian Inst. Ann. Rept. 1909, pp 225–36 (1910)

mentioned F. G. Cottrell, A. B. Lamb, R. C. Tolman, Graham Edgar, S. C. Lind, A. T. Larson, H. A. Curtis, J. M. Braham, W. C. Bray, J. A. Almquist, and F. A. Ernst.

Soda

Under this heading Dr. J. L. Smith discussed at length the Le Blanc process, which is now a vanishing one and one which never gained a foothold in the United States. He gives an interesting chronological table of the progress of the soda industry from 1790, when soda was obtained from barilla and kelp; refers to cryolite as a source; and mentions the recent perfecting of the bicarbonate of ammonia process by Solvay & Company of Belgium who, in 1873, produced 5000 tons of soda by this process. At the census of 1923, 1,707,987 tons of soda ash were returned, of which 1,674,234 tons were produced by the ammonia-soda (Solvay) process, to which are added 33,753 tons of "natural and electrolytic soda." The production of soda from natural brine was thoroughly investigated by Chatard,[1] while J. D. Pennock was an active factor in the development of the ammonia-soda process in this country.

Potash

According to Wilbert,[2] the Jamestown Colony, as far back as 1608, produced pot or soap ashes which were shipped to England. Although Henry Wurtz in 1850 found that considerable quantities of potassium existed in our greensand marls and described processes for its extraction, wood ashes, except for India saltpeter, remained the chief source of potash and potassium compounds until the extraction of the latter from the abraum salts of the Stassfurt deposits began, about 1861. In that year we imported from this source the potassium chloride used to produce, by metathesis with sodium nitrate, potassium nitrate for the gunpowder used in the Civil War.

At about this time our fertilizer industries, started in 1850 for the treatment of guano and coprolites, began compounding fertilizers, and they found their potash in Stassfurt salts. This source was so fostered that our native industry sank from a value of $1,401,533 in 1850 to $104,000 in 1905, while in 1913 we imported potash salts to the value of $13,200,413. Therefore in 1914, on the breaking out of the World War, we were so dependent on these foreign sources that when commerce was inter-

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[1] Chatard, T. M., "Natural Soda; Its Occurrence and Utilization," U S. Geol Survey, *Bull.* 60 (1888).

[2] *J. Franklin Inst.*, 157, 366 (1904).

rupted our condition was desperate. Steps were taken at once for governmental surveys of the country's potash resources, which were found not only in wood ashes but also in many minerals, such as greensand marl, alunite, leucite, feldspar and shales, in kelp, in surface brines and their deposits, likewise in industrial wastes from the manufacture of sugar and alcohol, and in the dusts from blast furnaces and cement mills. The story of effort and accomplishment has been admirably told by J. W. Turrentine in his recently published book[1] in which he says:

> It was the threat of the late German Empire that, because of the potash monopoly which it held, the world could be subjected at its will to potash starvation and be forced to yield to its dictation. This challenge was met in America by the prompt development of practically all of the sources of potash already surveyed by governmental agencies and the establishment of potash manufactories which made America, for the time being, independent of all foreign potash. The effect on the outcome of this world-wide imbroglio of this show of spirited aggressiveness on the part of America cannot be determined, as its value is inestimable.

Naturally the success of the different undertakings varied with various conditions, such as the nature, the richness and the ease of access to the raw material, and on the nearness of the factory to its market. The outstanding successes were those of the U. S. Industrial Alcohol Company, using the process of M. C. Whitaker; the Santa Cruz Portland Cement Company, using the Krarup process; the sugar companies, using the Steffens process; and the American Trona Company, working the brine of Searles Lake, California. The last-named plant is the largest single potash producer that has resulted from American efforts to establish a domestic potash industry. It was one of forty-four plants engaged primarily in the production of potash, and the only one to survive under peace-time conditions. Dr. Turrentine remarks of this:

> The American Trona Corporation, the company that had devoted the most time and effort to fundamental chemical research, was the one that was enabled to continue in operation. The continued development of its processes, cheapening its manufacturing costs and improving the quality of its products, has enabled it to survive successfully the post-war period characterized by exceedingly severe economic conditions.

The researches, through which this brilliant result was achieved, were planned and directed by John E. Teeple, the very efficient Treasurer of our SOCIETY.[2]

Gas, Illuminating and Heating

This legend embraces both manufactured and natural gas. The former, as an industry, began in April, 1812, with the granting

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[1] Turrentine, J. W., "Potash. A Review, Estimate and Forecast," John Wiley & Sons, N Y, 1926.

[2] Teeple, John E, "Research: Its Position in the Making of an Industry," *J Ind. Eng. Chem.*, **14**, 904 (1922).

of a royal charter to the Chartered Gas, Light, and Coke Company of London, England. It may be recalled that, at its Washington meeting in 1911, the AMERICAN CHEMICAL SOCIETY set on foot the celebration of the centenary of this event, that in consequence joint meetings were held April 18 and 19, 1912, at the Franklin Institute, with that institution, the American Philosophical Society, and the American Gas Institute. The record of this event, with all its attending circumstances, was published in the *Journal of the Franklin Institute* for that year and by the American Gas Institute as a separate volume. This was followed by the enormous and profusely illustrated "Gas Jahrhundert Nummer" of the *Leipziger Illustrirte Zeitung;* a gas exposition at Antwerp; and finally, a brochure of 92 pages, beautifully gotten up under the direction of Sir Corbet Woodall, governor of the company, entitled "The Gas Light and Coke Company 1812–1912." The industry began to supply coal gas in this country with the chartering of a gas company in Baltimore in 1816.

A marked change came about in the seventh decade of the century through the combining of the cupola retort system of Tessie du Motay with the generator-superheater system of T. S. C. Lowe for the manufacture of carbureted water gas, and especially in having available, at low cost, an abundant supply of petroleum distillates and residues for use as carburetors. At about the time our SOCIETY was formed this industry had attained a secure foothold and since then cognizance has had to be taken of water gas, carbureted water gas, and mixed coal and water gas. In the meantime, with the introduction of the by-product coke ovens, the richer gas from these devices, as well as that from retorts, has been sent out in the public service mains. Following Willson's development of the electrothermic method for the production of calcium carbide, acetylene became available as an illuminant, at first for individual and isolated installations, but later for distribution in small communities.

With the introduction of the incandescent electric lamp in 1879, the use of coal and water gas as an illuminant was seriously jeopardized. Fortunately, however, Edison's development was closely followed by the results of Auer von Welsbach's application of his discovery of the remarkable behavior of the oxides of the rare-earth metals with flames, through which he invented the incandescent gas mantle and made it possible to obtain, with low candle power, manufactured coal and water gas, and with natural gas, illuminating effects comparable with those from electric lamps. As a result of this, and of the greatly extended use of gas for heat and power, the criterion for gas has been very properly changed from candle power to thermal units. In the establishment of the mantle industry in this country and the solution of the many chemical and other problems, which arose in creating such an undertaking, credit is due Waldron Shapleigh, Harlan S. Miner, and M. C. Whitaker, while E. G. Love and W. H. Fulweiler have been most active in the chemical investigations of gas.

The industrial progress may, to a degree, be shown from the records of the census in that in 1876 the value of the products of "gas, manufactured" was about 40 million dollars, while in 1923 it was over 450 million dollars. These figures included not only gas but the by-products also. A special feature of the development of the half-century has been the perfecting of methods for the recovery and utilization of the by-products.

In making a study of the situation in 1909[1] I canvassed all available sources of gas in the United States and found the following quantities produced:

	Thousand-Cubic Feet
Gas industry	163,744,531
By-product coke industry	65,885,778
Natural gas	480,706,174
Producer gas	100,000,000
Blast furnace gas	*2,900,000,000*
Total	3,710,336,483

The Bureau of Mines reports the "natural gas consumed" in 1924 to amount to 1,141,482 million-cubic feet. It is not probable that the increase in the other items of the above table has been of the same order but for each it has been great. An interesting item in the Bureau's report is that, of the 1924 natural gas produced, 156,514 million-cubic feet were used in the manufacture of carbon black—a development with which the name of Samuel Cabot has been closely associated. Before the war the stripping of the cyclic hydrocarbons from the coke-oven gas of metallurgical works, in order that these hydrocarbons might be used in enriching gas served elsewhere for domestic purposes, had become established practice. During the war this practice was extended to domestic gas supplies to obtain the toluene and xylenes required for military purposes. The SOCIETY's representation on the Toluol Committee consisted of A. Bender, F. E. Dodge, W. H. Fulweiler, J. B. Hill, F. W. Sperr, Jr., and C. C. Tutweiler.[2] The stripping of natural gas to obtain the homologs

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[1] Munroe, Charles E , "The Gas Industry of the United States, 1909," *Progressive Age*, 30, 232–34, 274–77, 322–27, 368–73 (1912).

[2] "*Methods for Testing to Be Used in* Toluol Plant Operation," Ordinance Dept , U. S. A , 1918 The Toluol Committee was appointed by the War Department

of methane has now become common, such hydrocarbons being chlorinated and many subsequently hydrolyzed to produce alcohols which, again, form the parent substances for other chemical products. This industry is growing so fast that natural gas, used as a source of chlorinated compounds and alcohols, may soon become a separate item in our enumerations. In the cracking of petroleum in the water-gas carburetor, or elsewhere, unsaturated, as well as saturated, hydrocarbons are produced, and these[1] form other starting points for chemical manufacture.

By-Product Coke

This industry is practically an imported one. The first known mention of the utilization of by-products from coking in the United States is the statement in the census reports of 1880 that the Consolidated Gas Company of Pittsburgh collected the gas from beehive ovens and distributed it for lighting purposes. The first plant of modern by-product ovens built in the United States was a battery of twelve Semet-Solvay ovens erected at Syracuse, New York, in 1892. This installation demonstrated the value of by-product coking, and the number of ovens increased to such an extent that the total value of their output for the year 1904 was returned as $53,455,108, of which over $3,150,000 was the value of the by-products. In reviewing these returns I made[2] an estimate of the gain which would have resulted if all the coal which was coked during the census year had been treated in by-product ovens (assuming, of course, similar yields and unit values for the beehive coal coked, which naturally might not hold true) and found it to amount to over $37,000,000.

The total value of the products of the coke industry for the year 1923 was $516,922,898, of which $153,100,896 was for the by-products. Of the 19,640,798 short tons of coke produced in 1899, 4.6 per cent was generated in by-product ovens; of the 25,143,288 tons of coke produced in 1904, 2,422,796 tons, or 9.6 per cent, were made in by-product ovens; whereas of the 56,017,325 short tons of coke produced in 1923, 36,637,455 tons, or 65.4 per cent, were the output of by-product ovens.

Since the Semet-Solvay ovens were introduced they have been greatly improved and many other forms, having special advantages, have been used. Notable among these are the Otto Hoffmann, the Koppers, and the Becker ovens. The products of the by-product coke industry are similar in kind to those of the gas

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[1] Kirkpatrick, S. D., "Commercial Production of Isopropyl Alcohol," *Chem Met Eng.*, **33**, 402–3 (1926)

[2] Munroe, Charles E., "Coke," Census of Manufactures, 1905; *Bull.* **65** (1907).

industry. Today each of those from the coke industry exceeds in amount the same kind of product from the gas industry. For instance, the quantity of ammonia (in all states of combination) produced in the coke industry in 1923 was 287,681,592 pounds, while that produced in the gas industry was only 22,749,950. Among those prominent in this development may be noted J. D. Pennock, F. W. Sperr, Jr., and William Hutton Blauvelt.

It is recognized that the character and yield of products from the carbonization of coal depend not only on the character of the coal treated but also on the conditions under which it is thermolyzed. In recent years much study has been given to low-temperature carbonization and among others, engaged in this investigation, S. W. Parr has been most prominent.

Petroleum Refining

It may well be pointed out that the splendid petroleum industry of the United States (as well as those of other countries modeled on it) was initiated through the researches of an American chemist, Benjamin Silliman, Jr., who, under date of April 18, 1855, rendered his "Report on the Rock Oil, or Petroleum, from Venango County, Pa.," giving the results of his investigation of the chemical and physical properties of this petroleum. Boverton Redwood, the English authority, says:

> The first to undertake the systematic examination of petroleum, and some of the commercial products obtained from it, was Prof. B Silliman, Junr * * * * He fractionated the crude oil by distillation, and on examining the distillates, he came to the conclusion that certain of the bodies which they contained were products of distillation, and were not present in the crude oil. Professor Silliman studied the action of various reagents on the fractions, the behavior of the distillates when cooled, the value of the different oils as illuminating agents and lubricants, and their suitability for employment as a source of gas.

A graduate of Yale, Silliman was appointed professor of applied chemistry there in 1846. He was one of the founders of the Sheffield Scientific School in 1847 and professor of medical chemistry and toxicology at the University of Louisville 1849–1854. He was in charge of the departments of chemistry, mineralogy, and geology at the World's Fair in New York in 1853, and in 1854 he succeeded his father as professor of chemistry at Yale, which position he held until his death in 1885.

Silliman's researches, the results of which were embodied in the above-mentioned report, were made on seepage material. Accounts differ as to his relation to the actual search for the oil deposits. It is stated that a company, styled the Pennsylvania

Rock Oil Company, was formed with Dr. Silliman as president, that it acquired rights over a considerable area in Venango County, but that it was unsuccessful in its attempts to locate oil. That, later, the "New Haven stockholders" in this company formed the Seneca Oil Company, obtained access to a portion of the territory of the Pennsylvania Rock Oil Company, and employed E. L. Drake to sink wells for them. That he conceived the idea of driving an iron pipe to overcome the obstacles encountered, and that on August 28, 1859, he struck oil on Watson's Flats, near Titusville, Pennsylvania.

The growth of the industry of petroleum refining, largely because of the information furnished by Silliman, was rapid, and many chemists became engaged in the study of petroleum and its products. Notable among them was Cyrus M. Warren, for a time professor at the Massachusetts Institute of Technology, who devised much apparatus and many methods for the study of fractional and destructive distillation, and the products of these processes. At first alone, and then in collaboration with F. H. Storer, he published extensively on the "Volatile Hydrocarbons." Contemporary with Warren was S. F. Peckham, for a while professor at the University of Minnesota. He had entered the Army following his graduation from Brown and, in 1866, was chemist to the California Petroleum Company. He then began his studies of petroleum and bitumens, which he continued throughout his life. He was the author of that stupendous Report on Petroleum in the United States Census of 1880 which has proved a mine of information for Redwood and all subsequent writers on the subject. These researches on the constitution of petroleum were continued in a most able manner by Charles F. Mabery, of the Case School of Applied Science. It is of interest that this early work in this field was aided by allotments from the C. M. Warren fund of the American Academy of Arts and Sciences.

Older members will recall the active controversy that "lit up" the pages of THE JOURNAL for a considerable period between Peckham and Clifford Richardson (to whom the world owes much in the development of asphalt pavements), over the constitution of bitumens. Both men were positive, forceful characters with very different outlooks. It did not tend to soften the asperities that there was a marked disparity of age and that Peckham had addressed the National Academy of Science on bitumens nearly a decade before Richardson's graduation from Harvard. Moreover, a commercial element appeared in that

Koehne-Williams

JOHN J. MILLER
(1887–)
Editor, *Chemical Abstracts* 1914

EVAN J. CRANE
(1889–)
Editor, *Chemical Abstracts* 1915–

Underwood & Underwood

MILTON C. WHITAKER
(1870–)
Editor, *Industrial & Engineering Chemistry* 1911–1916

HARRISON E. HOWE
(1881–)
Editor, *Industrial & Engineer- Chemistry* 1922–

Richardson represented the manufacturer and contractor, while Peckham now was advisor to the City of New York and perhaps other municipalities.

It was but a short time after petroleum refining began that kerosene practically displaced whale oil, camphene, and other illuminants in use, except coal gas in communities of sufficiently dense population to permit its being distributed at a profit. It is true, "gasoline and naphtha" were burned to a slight extent in "sponge" lamps and used as solvents, as vehicles in paints, and for other purposes, but as kerosene commanded the higher price and was more readily sold there was a constant temptation to run the more volatile hydrocarbons into the kerosene "cut," thus producing low flashing-point oil. The result was that fires and explosions from the use of kerosene lamps were appallingly frequent until C. F. Chandler began his trenchant, and successful, campaign for the regulation by law of kerosene. He was aided by the development of gasoline-gas generators; by the growth of the water-gas industry, in which petroleum crudes and side products were used as carburetors; and particularly, by the automobile with the Selden engine becoming, in 1894, an accomplished fact.

The use of gasoline and of lubricants for automobiles, motor boats, and later for farm machinery, airplanes, and dirigibles, created not only an enormous demand for these substances but also for crudes for their production. Among extensive deposits of oil located and tapped were some, like that at Lima, Ohio, and in Canada and California, so high in sulfur content as not to be amenable to established methods of refining. Herman Frasch devised an operative means for the removal of this sulfur, and thus made such crudes available.

The normal gasoline yields, even aided by such cracking as the stills then in use permitted, not being enough to meet the demands, resort was had to the recovery of casing-head gasoline and then to stripping natural gas, W. O. Snelling and C. A. Burrell being pioneers in this art. The demand still growing, processes were developed for cracking under high temperatures and pressures, the Rittmann process being a type of the treatment of the petroleum in the vapor phase, and the Burton, Dubbs, and others of that in the liquid phase. The latter appears to be in successful operation.

In gasoline engines it is desired to obtain a high rate of combustion of the mixture in the cylinder, but when the rate of reaction passes from that of combustion to that of detonation knocking occurs and efficiency is impaired. In a model investigation, Thomas Midgley, Jr., and his associates found quite a number of substances which, when introduced into the mixture, prevented this change of rate. Among these they selected tetraethyl lead as the most efficient and practicable antiknock substance. This has been used successfully on an extended scale, but unfortunately, being very poisonous, it gave rise to fatal accidents during manufacture, which caused its withdrawal from the market and an investigation of the circumstances by a committee of experts acting under the United States Public Health Service. This committee has found that the handlers and users can now be properly safeguarded and "Ethyl Gas" has again come into use.

The magnitude which this industry has attained since 1859 is enormous. In 1925 the world's production of petroleum was over 1,060,000,000 barrels, of which the United States produced 764,000,000 barrels. There were refined in the United States 740,000,000 barrels, of which 41,338,000 barrels were imported. The output of gasoline was 10,886,127,000 gallons, of which about one-fifth was produced by cracking processes and one-tenth was natural gas gasoline. The quantity of kerosene produced was 2,510,334,000 gallons, or but about one-fifth that of gasoline. In 1880 the output of kerosene was about twenty times the volume of the gasoline. The consumption of our petroleum is advancing so rapidly that other sources of liquid fuel must soon be sought. One immediate source of supply is indicated in the oil shales[1] which were investigated by Charles Baskerville and W. A. Hamor in 1909.

Explosives

High explosives, in the person of nitroglycerol, first appeared in the census of 1870, six years prior to the founding of this Society. For some five hundred years prior to that time man's demands for propellants and blasting agents had been met by black powder mixtures (gunpowders and blasting powders). Dr. Smith, in his Northumberland address, also mentions guncotton, but the manufacture of military guncotton began in this country at a later date and never rose to any considerable magnitude. In 1870 the value of black powder manufactured was $4,011,839, and of nitroglycerol $225,700, or a total of $4,237,539. In 1923 the total value of the products of this industry was over $75,000,000. The total quantity of explosives made in 1923 was

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[1] See also the work, "Shale Oil," by Ralph H. McKee of the American Chemical Society Monographs

577,245,570 pounds: of these 262,290,012 pounds were dynamites; 67,334,759 permissibles; 2,695,780 nitroglycerol used directly as an explosive; 8,433,986 (25-pound) kegs of blasting powder; 2,779,422 pounds of black gunpowder; 5,150,825 of smokeless powder; 2,724,300 of fuse powder; and 23,420,822 pounds of "all other explosives." The peak of production for black powder was reached in 1907, when some 287,000,000 pounds were manufactured.

Russell S. Penniman made a most important contribution to the industry in 1885 when he introduced the coating of ammonium nitrate, to check its hygroscopic action, for use in explosives, ammonia dynamites, and ammonia-gelatin dynamites being now quite widely used. A large amount of weak nitric acid recovered from spent acids and other sources is utilized in making ammonium nitrate. In 1925 over 71,000,000 pounds of ammonium nitrate were used as an ingredient of explosives.

Permissible explosives are such as have passed the chemical and physical tests prescribed by the United States Bureau of Mines to determine their suitability for use in coal mines, where explosive atmospheres of gas, or dust, or both, with air may occur. They originated from the investigations of the "causes of mine explosion" authorized by the Congress in 1908. Among those most active in these investigations are Clarence Hall, W. O. Snelling, C. G. Storm, S. P. Howell, J. E. Crawshaw, G. St. J. Perrott, and C. A. Taylor. The chemical researches of E. J. Hoffman and W. H. Rinkenbach are of especial value. The writer has had close association with this work from its inception.

The success of a manufacturing enterprise depends, among other factors, upon its freedom from accidents that interrupt its operations and destroy its property. The explosives industry is obviously exposed to many hazards and especially in transportation. On the advice of Charles B. Dudley, chief chemist of the Pennsylvania Railroad Company, the American Railway Association in 1905 appointed a committee consisting of Charles E. Munroe, chairman, Henry S. Drinker, and Charles F. McKenna to investigate and report on the regulation of transportation by rail so as to reduce liability of accidental explosions. Following the rendering of the committee's report,[1] the Bureau for the Safe Transportation of Explosives and Other Dangerous Articles was established and Beverly W. Dunn was appointed chief inspector. So efficiently have the duties of this office been performed that in his annual report, March, 1926, he was able

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[1] *Am Ry Assoc Circ* **615**, 13–15 (September 21, 1905)

to say that although over 500,000,000 pounds of explosives were transported by the railroads of the United States and Canada during the calendar year 1925, but twenty-six accidents, causing a property loss of $11,702, occurred, and no casualties whatever resulted. In fact, a distinguishing feature of the past fifty years has been the safeguarding of operations and operators, and chemists have been leaders in the safety campaign.

Prominent among the many who have been active in the development of explosives are George M. Mowbray, Walter N. Hill, Lammot du Pont, Charles L. Reese, G. C. Hale, Fred Olsen, A. M. Comey, and Tenny L. Davis. The full story is to appear shortly in a work prepared under the auspices of the Institute of Makers of Explosives.[1]

This review would be incomplete without reference to the abnormal activities of the explosives industry during the World War when fifty-three new plants, involving an expenditure of more than 350 million dollars, were constructed and put into operation in eighteen months. Production of TNT, amatol, picric acid, explosive D, tetryl, TNA, and smokeless powder was conducted on a previously unheard-of scale, but this and other achievements, in the applications of industrial chemistry to warfare, have already been most fully recorded.[2] Conspicuous in this war development was the large-scale production of poisonous gases under the efficient efforts of W. H. Walker and in which W. L. Lewis rendered distinguished services. The story of the development of this industry and of the organization of the Chemical Warfare Service as a unit of the Army has been told by Fries and West.[3] Speaking of the latter, the authors say, "This holds the distinction of being the first recognition of chemistry as a separate branch of the Military Service in any country or in any war."

Plastics

The discovery of the colloidal solution called "collodion" was made by Maynard, of Boston, in 1847. It was in 1874 that L. S. and J. W. Hyatt reduced to practice the method employed in the manufacture of that pyroxylin plastic which they styled "celluloid." Chemical progress in this industry was due largely to J. H. Stevens. Another important development was the single base smokeless powder in which use was made of May-

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[1] Van Gelder, A. P., and Schlatter, Hugo, "History of the Explosives Industry in America."

[2] Clarkson, Grosvenor B., "Industrial America in the World War," and Crowell, Benedict J., "America's Munitions."

[3] Fries, Amos A., and West, Clarence J., "Chemical Warfare."

nard's ether-alcohol mixture, though in different proportions, for the production of the pyroxylin colloid. In both the manufacture of collodion and of smokeless powder the cellulose nitrates employed are carefully chosen and are of a definite nitrogen content and viscosity-producing capacity. Much of the success in the development of this smokeless powder manufacture is due to Charles F. Burnside.

Another advance is in the gelatinization of cellulose nitrates of medium nitrogen content by nitroglycerol, or other nitric esters, to form explosive gelatin, from which, by admixture with wood pulp, sodium nitrate and other "dopes," gelatin dynamites result. Still another application was Chardonnet's squirting of this collodion into threads, the denitration of these threads, and their conversion into artificial silk. Again we have Archer flowing glass plates with this collodion for use in the wet plate process of photography, and within the last fifty years the Kodak Company, the Celluloid Company, and others forming from collodions containing acetone, and various other solvents, long continuous films for use in modern photography. We owe much of the chemical advancements in the photographic art to H. Carey Lea and C. E. K. Mees. Yet another development has been the production of collodion-like products from cellulose nitrates, with a wide variety of solvents, known as lacquers, or, when admixed with pigments, as enamels.

Plastics have come into commerce produced from casein, gelatin, fibrin, caoutchouc, gluten, resins, and other substances. The most modern and important are the phenol-aldehyde condensates, of which bakelite, invented by Leo H. Baekeland, is the most important. It will be recalled that he also invented the very valuable Velox paper printing process.

The statistics of the substances classified as plastics are subject to variation, yet some measure of growth may be gained by noting that in 1880, the first census in which these substances appeared, the value returned was $1,261,540; in 1900 it was $2,864,044; and in 1923 it had increased to $102,229,807.

Rayon

Attention has been called to Chardonnet's process for the production of artificial silk from cellulose through cellulose nitrates. In Germany this adaptation of cellulose was effected by the use of cupric ammonium compounds, whereas in England, Cross and Bevan effected the transformation through the formation of cellulose xanthate, inventing what is known as viscose.

All of these methods of producing artificial silk, now by requirement of the Federal Trade Commission called "Rayon," are in active operation in this country. The establishment of the viscose manufacture on a firm foundation is largely due to the investigations and supervision of our eloquent former President A. D. Little. Brought to public attention at the Paris Exhibition of 1889, this is now a firmly established industry. The output for 1925 was 197,000,000 pounds, of which 50,000,000 pounds were produced in the United States, which is now the leading producer. According to William J. Baxter,[1] speaking for the United States, "we have this new industry returning more profits during 1926 than the entire cotton industry." This is a marvelous achievement of industrial chemistry.

During the World War, to meet the demands for smokeless powder, successful investigations were made into the production of cellulose from wood. These results are at the disposal of rayon manufacturers, and the progress is such that wood may drive cotton from the market. This would be most deplorable for the resources of our forests are already overtaxed. The source of the cellulose should be found in annuals.

Paints and Varnishes

This industry is a very old one. At the census of 1850 the value of its products was placed at $5,466,052; from the average of the returns in 1870 and 1880 the value of its products fifty years ago was about $26,000,000. At the census of 1923 the value returned was $440,564,618. Among the novelties in the development of this industry are "ready mixed paints," with a value in 1923 of $147,000,000; zinc oxide, $23,471,098; lithopone, $13,001,506; and pyroxylin lacquers and enamels, $6,944,306. The production of the latter is growing more rapidly than perhaps any other member of the paint and varnish class. The automotive industry is a large consumer of lacquers, and the railroads are now testing them out on their rolling stock. They possess the advantage that they may be readily applied with the air brush or spray gun. The walls and wood work of the Book-Cadillac Hotel, at Detroit, containing one thousand two hundred guest rooms besides dining, ball, and lounge rooms and lobbies, have been sprayed with pyroxylin lacquer. Certain iron oxides, titanium oxide, and lead oxysulfates have come forward as pigments.

Among those responsible for advances in this industry are

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[1] Baxter, William J., "The American Industry 'Settles Down,'" *Manchester Guardian, Commercial* (April 15, 1926).

sturdy A. H. Sabin, Maximilian Toch, Victor Bloede, and Peter Fireman. The late Senator E. F. Ladd played an important part in fixing standards, while the researches of C. B. Dudley and F. N. Pease, of the Pennsylvania Railroad, revealed the useful parts played by barytes and other supposed make-weights. H. A. Gardner, in presenting the results of his researches on behalf of the Paint Manufacturers Association, is perhaps the most voluminous writer in this field.

Rubber

The rubber industry of today is a native development, beginning with the invention of vulcanization by Charles Goodyear in 1839. It is true that shoes of raw rubber had been imported or manufactured prior to that date, and their sale continued while Goodyear's invention was being commercially developed. I remember wearing such shoes, when I was quite small. They were heavy, clumsy, and resilient. We were truly bouncing boys on the days when we wore these rubber shoes. I remember, too, how these unvulcanized rubbers became soft and sticky in summer. The industry has improved to the extent that competent chemists and chemical engineers have been put in control of plantation and factory processes, and have been given an opportunity to conduct researches into the constitution and behavior of rubber. Caoutchouc being a terpene, all researches on terpenes have contributed to the advancement of this industry.

Rubber was brought from Para, in Brazil, to Salem, Massachusetts. The method of recovering the rubber from the latex, followed in Brazil (by gathering it on a stick and smoking it over a fire) reminds me in its crudity of the method I found in use in the art for pickling copper sheets while I was investigating the corrosion of the copper sheathing of the U. S. S. Juniata.[1] This consisted in scrubbing the sheets with the fermented urine collected from the operatives. I have learned of other gross, unscientific, and filthy practices transmitted through long periods in the empiric arts.

With the establishment of plantations the chemist was called upon for aid, with the result that the methods of separating the rubber from the latex practiced on the plantations are cleaner and better, and the product reaches the manufacturer of rubber articles in a purer condition. Kelly says:[2] "Today more than 75 per cent of the world's rubber supply is prepared under the scientific control of the chemist."

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[1] *Proc U. S. Naval Inst*, **12**, 319–417 (1886).

[2] Kelly, W. J., Chemistry in the Rubber Industry, "Chemistry in Industry, " Vol I, **1924**, pp. 340–56.

Not long after the vulcanized rubber industry became established, Clapp started a plant for reclaiming rubber at Hanover, Massachusetts. In 1900 the quantity of rubber reclaimed for re-use amounted to 40 million pounds. It is believed that this is one of the earliest instances of recovering waste in manufacture outside of the obvious one of remelting old metals.

Much investigation has been given to vulcanizers; to the use of sulfur chlorides, through which the "cold" as well as the "hot cure" has been developed; to the effect of a variety of substances as "dopes" or fillers; and, of recent years, to accelerators. Time, upon which interest fattens and through which output and turnover are impeded, is the essence of manufacture and merchandizing. The chemist has speeded operations so that, by the addition of 1–1.5 per cent of an accelerator to a mixture, the vulcanization may be speeded up from three hours to as many minutes for its completion. Accelerators are found among complex organic substances, such as aniline derivatives or substituted ureas. Among recent achievements is the decoagulation of coagulated rubber by William Beach Pratt, who has also been successful in effecting rubber dispersions. Among those who have contributed to the advancement of this industry, by their researches, are H. C. Pearson, W. C. Geer, and J. B. Tuttle. The value returned for rubber products at the census of 1923—$958,518,000—gives but a partial view of the consequences of Goodyear's comprehension of the meaning of his "cut and try methods," for the industry has attained enormous proportions in many foreign countries. It is well to note that the automobile industry rests on rubber.

Essential Oils and Perfumes

These are of natural origin, like the oil of peppermint, or artificial, like heliotropin. Many of them contain esters, but aldehydes and ketones are frequently present. They are used as perfumes, in flavoring, and as therapeutic agents. The industry is, in the monetary value of its products, a minor one, but it plays an important role in the life of man. The total value of its products in 1899 was $434,451. In 1923 this had risen to $3,393,720. This industry is indebted in many directions to F. B. Power, distinguished for his researches on chaulmoogra oil; also to Edward Kremers, Clemens Kleber, and E. K. Nelson, who have investigated the character of the oils from many natural sources; and to Alfred Springer, who has mastered synthetic flavors. None who have heard or read it can forget M. T. Bogert's masterly address on perfumes. A leader in the field of peppermint oils was A. M. Todd, a former active member of this SOCIETY, and for some time a member of Congress.

Fine Chemicals

This is a class which one finds particularly difficult to define and delimit. Evidently pure, and especially synthetic, "essential oils" might be gathered here. Bulletin 210 of the Census of 1900 says:

> Under this classification are grouped the chemically pure chemicals manufactured for sale, the chemical substances which are made for use in laboratories and in pharmacy, and those in which, like the salts of silver and of gold, the price of the unit of measure is relatively very high.

Dr. McMurtrie rather shook my foundations when, as chief chemist of the Royal Baking Powder Co., he said, with glistening eyes, "We are now turning out cream-of-tartar 99.95 fine regularly in tonnage lots." Similar progress has been made by others in the manufacture of some "General Chemical" on a large scale of a high degree of purity. Dr. Herty has recently written a charming article[1] covering many substances in this class. In this group also are included organic solvents which, in recent years, not only have increased largely in volume but also have multiplied in number. These solvents not only are of immense importance in effecting analytical separations so that each new solvent possesses much potential power in solving problems, as indicated by the researches of Victor Lenher with tellurium and selenium, but they also enter into a multitude of industries, such as in the separation of alkaloids from their natural occurrences; as vehicles in paints, varnishes, lacquers, and enamels; for use in the production of colloids and colloidal solutions; and for a great variety of other purposes.

This subject has been recently developed by D. B. Keyes.[2] He very properly places ethyl alcohol first for, with the exception of water, no solvent is so widely used. It is also an important parent substance in farther manufacture. It was long recognized that an important factor in giving Germany dominance in many of the chemical industries, and more especially those producing organic chemicals, was that her government had made alcohol tax-free for use in the arts, while our Government and others had not done so. Finally, our legislators awakened to the gravity of the situation. In 1906, being summoned before the com-

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[1] Herty, Charles H., "The Future of the Synthetic Organic Chemical Industry in America," *J Chem. Education*, **2**, 519–32 (1925).

[2] Keyes, D. B., Alcohol and Some Other Solvents, "Chemistry in Industry," Vol. I, **1924**, pp 34–57.

mittee of our Congress dealing with tax-free alcohol for use in the arts, I well recall Mr. Volstead's earnest advocacy of enacting legislation to that effect, and in 1907, being appointed superintendent of the Special Alcohol Exhibit at the Jamestown Exposition, designed to promote the purposes of the Act of Congress of June 7, 1906, and subsequent legislation of this kind, I have naturally followed succeeding events with special interest. I believe I express the feeling of all who have the welfare of the chemical industries, and the people they serve, at heart in saying that it is much to be regretted that so wise and beneficent a piece of legislation should be greatly nullified by bureaucratic regulations.

An important development in this field was the large-scale production of furfural, from corn cobs, oat hulls, and similar waste materials, which resulted from the investigations of F. B. LaForge and his associates in the United States Department of Agriculture. A marked novelty was the fitting out of the "S. S. Ethyl" as a factory in which to extract bromine from the sea water in which the vessel floats. Another novelty is the large-scale production of absolute alcohol; also that of synthetic ethylene glycol, which is displacing glycerol in the explosives industry.

This country owes much to E. R. Squibb, J. Uri Lloyd, G. D. Rosengarten, Eli Lilly, G. P. Adamson, and many others for developing this industry and keeping abreast of progress but, as pointed out, largely because of special privilege, before the World War our manufacturers were unable to compete in the market for a large line of these products. When the war broke out in Europe and we were deprived of many essential chemicals of this class, C. G. Derick inaugurated a small-scale plant at the University of Illinois, which has been continued by Roger Adams,[1] that alleviated the situation. Actual manufacture in this field was begun by the Eastman Kodak Company in 1918, followed by the Heyl Laboratories, Special Chemical Company, and the Synthetic Laboratories. In 1923 the Eastman Company listed over 1300 different fine chemicals, and probably more than 2000 are now available.

In the census of 1900 the products in this class were valued at $4,216,744. This classification does not appear in the report for 1923, but on assembling the separate items from the records I find the value to be over $81,000,000.

Other Industries

Limitations of space compel but brief mention of other industries such as fertilizers, whose production in 1914 was valued

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[1] Clarke, H. T., "Rare Organic Chemicals," *J. Ind. Eng. Chem*, **14**, 836–37 (1922).

at $153,196,000, and in 1923 at $183,089,000; tanning materials and natural dyestuffs at $20,620,000 and $35,972,000, respectively; soap at $39,075,000 and $102,857,000; and wood distillation and charcoal manufacture at $10,284,000 and $29,695,000. Coal-tar products have fluctuated greatly, but for 1923 the value returned was $143,783,985.

Dr. J. Lawrence Smith in his 1874 address devoted considerable space to "Stearinery," including soap, stearic acid, glycerol, and related material. It is pointed out that the glycerol industry owes much to the researches of R. A. Tilghman, of Philadelphia. More recently Ernst Twitchell has reduced to practice a catalytic fat-splitting process for the production of fatty acids and glycerol. During the war John B. Eoff, W. V. Linder, and G. F. Beyer, chemists in the Internal Revenue Bureau under chief chemist A. B. Adams, developed a successful process for producing glycerol from black strap molasses, using preferably as the fermenting organism *S. Ellipsoideus* (var. *Steinberg*). W. O. Snelling sought to obtain glycerol from trichloropropane, prepared from the propane of natural gas, but this had not been reduced to practice when the war ended.

The researches of William McMurtrie, H. W. Wiley, F. K. Cameron, and the chemists at many of the agricultural experiment stations and colleges contributed much to the fertilizer industry. It is to be regretted that records of Dr. Wiley's early extensive researches in this field at the Bureau of Chemistry were withheld from publication.

Food products is another large industry which, in recent years, has been greatly promoted by the researches of chemists. Notable in this field are H. W. Wiley, C. L. Alsberg, and C. A. Browne. This industry offers in the Research Laboratories of the National Canners Association, organized in 1913 under W. D. Bigelow, an admirable example of the benefit of coöperative research under competent and judicious direction.

Among the many ramifications of the food products industry is that of dairy products, which is much indebted to S. M. Babcock, of the University of Wisconsin. In his memorial notice of E. N. Horsford, inventor of phosphate baking powder, of an emergency ration for troops in the Civil War, and sometime professor of chemistry at Harvard, C. L. Jackson[1] says that Horsford invented condensed milk, which he worked out for use in Dr. Kane's Arctic Expedition that sailed in 1853. Gail Borden appears to have been investigating this field at about

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[1] *Proc Am. Acad Arts Sci*, **20**, (N. S.), 340–61 (1893).

the same time. Whatever be the truth as to priority, it appears evident that the industry of condensed milk originated in this country. Evaporated milk was first packed in this country on a commercial scale in 1885, and this was followed by spray drying to produce powdered milk.

Another American industry is that of cottonseed oil, which started in a small way in Columbia, South Carolina, prior to 1826. Refining by caustic soda was introduced into the refineries in New Orleans between 1860–1870. The use of fuller's earth was worked out by William B. Albright and Henry Eckstein in 1880. In 1893 Eckstein accomplished deodorization by heating the oil to a high temperature and passing steam through it, while David Wesson put in operation at Savannah, in 1900, deodorization in a vacuum. Wesson[1] says:

> Chemistry has had the industry in hand since 1890. In consequence, refining methods have been improved greatly, losses have been prevented, and new products have been evolved. The process of hydrogenation has been particularly active in expanding the industry to its present great dimensions. The chemist has been the means of putting about $125,000,000 every year in the accounts of the farmer; in other words, he has added ten to twelve dollars to the value of the crop for every bale of cotton grown.

A similar tale might be written for the corn products industry in which Arno Behr won his spurs.

Forestry, Vegetable, Animal and Other Agricultural Industries

Little attention can be given to wood products, though they play an important part in many chemical industries, either directly as pulp in the manufacture of paper, dynamite, and other substances, or as a source of chemical substances like turpentine, rosin, many dyestuffs, tanning materials, and exudates such as balata, gutta-percha, caoutchouc, and gums for chewing and for varnishes. Large as are the number of known products from vegetable sources, the interesting production of mucic acid from the wood of the larch by S. F. Acree indicates that this mine is by no means exhausted. In fact, I am of the opinion that there are many more most valuable substances yet to be recovered commercially. The unexpected usefulness of the chemist in the forest products industry is illustrated in Charles H. Herty's invention of a cup for gathering turpentine from the long-leaf pine, which has greatly improved this wasting industry. H. O. Chute and M. G. Donk have been prominent in devising methods for the better utilization of the stumpage and improvement in distillation process by which a larger number of useful products

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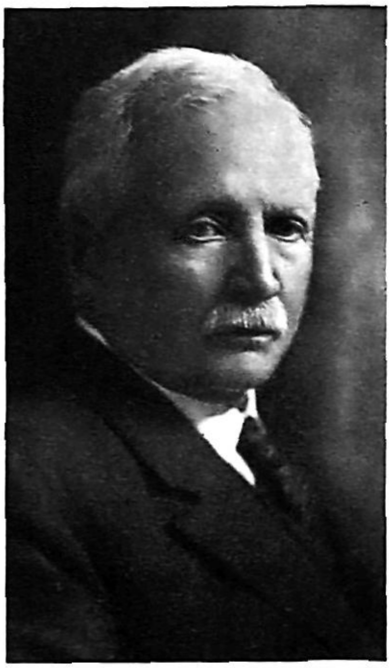
[1] *J. Ind. Eng. Chem.*, 7, 277 (1915).



Henry E. Niese
(1848–)
Charter Member

Alman & Co.

J. B. Francis Herreshoff
(1850–)
Charter Member

Alman & Co.

Samuel A. Goldschmidt
(1848–)
Member for Fifty Years

Adolph Kuttroff
(1846–)
Member for Fifty Years

S. A. Goldschmidt attended the Priestley Centennial in 1874.

have been obtained. The chemists of the Hercules Powder Company, under the leadership of George M. Norman, have been especially successful in putting new life into the utilization of southern yellow pine waste for naval stores. An important factor in promoting the improvements in commercial turpentine and rosin has been the work of F. P. Veitch and his co-workers of the United States Department of Agriculture, which led to the passage of the federal naval stores act in 1923.

The paper industry has particularly benefited because of the intimate knowledge of this industry possessed by A. D. Little, the ingenuity and indomitable perseverance of Hugh K. Moore, and the organizing ability of Robert B. Wolf. It is of interest that two of the important processes for paper making are of American origin—the sulfite process, invented by B. L. Tilghman in 1867, and the soda process, invented by Watt and Burgess in 1853. Of a somewhat analogous character is the utilization of sugar cane bagasse in the manufacture of artificial lumber to replace for certain uses white pine and other soft woods that are so rapidly disappearing. With the art reduced to practice by T. B. Munroe and C. G. Muench some six years ago, there are now produced over 17 million square feet of lumber per month. The application of chemistry and physics to the protection of the users of paper was first suggested and undertaken in this country at the Bureau of Chemistry. As a result of this, the Congressional Joint Committee on Printing has since 1912 purchased all paper for the Public Printing and Binding on carefully prepared specifications.

The federal Department of Agriculture, during the last half-century, has also made generous provision for the advancement of animal and plant industries through the chemical investigation of their special problems. Notable among these may be mentioned the researches of E. A. de Schweinitz and Marion Dorset through which the deadly hog-cholera was conquered. The researches of J. K. Haywood, C. C. McDonnell, H. H. Custis, J. N. Taylor, and other chemists of the department upon insecticides, and of V. K. Chesnut and J. F. Couch upon poisonous plants also deserve to be mentioned in this connection.

The great packinghouse industry, which is dependent upon agriculture, is of American origin and involves almost innumerable applications of chemistry in the solution of its problems. W. L. Lewis, Arthur Lowenstein, W. D. Richardson, Paul Rudnick, and L. M. Tolman are among the more prominent workers in this field.

The Chemist in Sanitation

Water is probably more important and quite as valuable as the product of any of the industries cited. The chemist has been most active in investigating potable water and water for industrial, manufacturing, and therapeutic purposes. Public service waters are brought into proper condition for sale by coagulation, sterilization, and softening. In 1875 there were 275 water works in the United States, whereas in 1926 there were over 9000. The most novel development was that of sterilization worked out at Chicago, Illinois, and Boonton, New Jersey, in 1908 with hypochlorite of lime and in 1910 with chlorine. Among those active in this field have been W. R. Nichols, W. D. Collins, J. W. Mallet, C. R. Darnell, A. M. Buswell, E. M. Chamot, F. R. Georgia, R. S. Weston, W. P. Mason, Edward Bartow, W. W. Skinner, and J. W. Ellms. Mrs Ellen H. Richards' chlorine surveys were especially ingenious and useful. C. F. Chandler's reports on the Saratoga waters were valuable contributions to knowledge. C. B. Dudley showed the value of the chemical supervision and treatment of waters, both for potability and steam generation, to railroads. W. P. Mason, Edward Bartow, L. P. Kinnicutt, and E. B. Phelps have also devoted attention to the chemistry of sewage, a closely related subject.

Another topic to which chemistry has contributed to a continually increasing extent, and especially since the introduction of water heaters and automobiles, is ventilation, more particularly with a view to the prevention of poisoning with carbon monoxide. Among examples of this are the studies of vehicular tunnels, and especially of the one projected under the Hudson River, by A. C. Fieldner, and of the New York subways by C. F. Chandler.

Research

A marked feature in the development of industrial chemistry during the last fifty years is the employment of educated chemists, at first in inspection and control work, and later in research work. Realizing what this meant to the industries, an inquiry as to the number of chemists employed was made, at the census of 1900, of each establishment reporting on "Chemicals and Allied Products." The total number reported as employed was but 276. An analysis, made by Secretary C. L. Parsons, of the membership of this SOCIETY, under date of October, 1924, discloses 2697 engaged in technical direction; 1236 in chemical development as research chemists; and 1167 in chemical control as works and laboratory chemists. It is not disclosed how many of the 1004 serving as executives, or of the 2423 in the managerial class, are trained chemists, but the number is large.

Much aid in industrial development has come from the professional chemist upon whom the manufacturer, in the early days, relied to get him out of trouble. The oldest of existing practitioners is probably the firm of Booth, Garrett, and Blair, founded in 1836 by J. C. Booth, the first man to be thrice elected President of this SOCIETY. His career has been set forth by Edgar F. Smith.[1] Space does not permit the naming of all practitioners but Rickett and Banks of New York, Mariner and Hoskins of Chicago, Arthur D. Little, Inc., of Boston, Pittsburgh Testing Laboratories, John E. Teeple of New York, S. P. Sadtler and Son, Inc., of Philadelphia, and the Industrial Research Laboratories, Washington, D. C., are among those well known to have engaged in development work. But the most outstanding feature of the latter part of the half-century is the inauguration of well-equipped research plants by manufacturers, such as the Hercules and du Pont explosives corporations, the General Electric Company, New Jersey Zinc Company, Eastman Kodak Company, and all corporations that desire to continue to do business. There are many instances in which industries as a whole have engaged in coöperative research, and this broad policy has commended them to those they serve.

The federal Government has contributed to this first, in the establishment of the Department of Agriculture with its widely known and most efficient Bureau of Chemistry and chemical laboratories in the Bureau of Soils and many other divisions, followed by the colleges of agriculture and agricultural experiment stations to each of which a corps of skilled chemists is attached. In fact agriculture, in its many ramifications, has received the aid of government chemists to a much larger extent than any other industry. Agriculture and other industries have also been served by the chemical staffs of the United States Bureau of Standards, Bureau of Mines, and Geological Survey.

A most beneficent outcome of the World War is the National Research Council which was created to organize, promote, and coördinate researches. Through the successive services of E. W. Washburn, W. D. Bancroft, F. G. Cottrell, J. E. Zanetti, J. F. Norris, and W. J. Hale, as chairmen of the Division of Chemistry and Chemical Technology, research in American chemical in-

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[1] Smith, Edgar F., "James Curtis Booth, Chemist 1810–1888," pamphlet, 1922, 17 pp

dustries has been greatly advanced. A recent example of the progress being made in this direction is the allotment of $100,000 per year for five years for research upon petroleum,[1] the program of which was arranged by the National Research Council.

Conclusion

As I review the foregoing I realize how much important material I have been compelled, through exigencies of time and space, to omit. The thrilling story of our synthetic dyestuffs industry, leather, glass, refractories, sugar, cement, iron and steel, and all the metallurgical industries, which are founded on and controlled by chemistry, have had to be passed by with many others.

In reviewing the phenomenal growth of industrial chemistry in America during the past fifty years it is natural to speculate upon the outlook for the future. Will the curve of accomplishment continue to rise at its present ascending rate or will it gradually flatten out in a horizontal direction? The peak of production with regard to certain important resources, that have played such an important part in the development of American chemical industries during the past fifty years, has already been passed. The supplies of natural gas, formerly regarded as almost unlimited and so lavishly wasted, are already approaching the point of depletion; one of the large sulfur wells of Louisiana has been exhausted; the annual yield of petroleum in the United States is diminishing and the untouched stores of anthracite coal are apparently nearing an end. The gradual exhaustion of these and other natural resources will tend to retard the development of our chemical industries with respect to certain of their present phases. With the depletion of our reserves we may look, however, to far greater improvements and economies in their chemical utilization. The resources of bituminous coal in the United States are still sufficient for many centuries and the utilization of these extensive deposits, not only for the generation of power and gas, but also as raw materials for the production of liquid hydrocarbons and other organic chemicals, will receive increasing attention during the next fifty years. There will also be a much greater utilization of water power as a source of electricity for chemical purposes, the recent developments at Muscle Shoals serving as a conspicuous example. Whatever the future may hold in store the American industrial chemist may be depended upon to render even more conspicuous accomplishments than those which have been so briefly reviewed in the present paper.

[1] "Proposed Research regarding Petroleum," *Mining and Metallurgy*, 7, 347–49 (1926)

CHAPTER XIII

CHEMICAL EDUCATION

BY SAMUEL R. POWERS

Chemistry has been an appropriate subject for study in the secondary schools since the development of the high-school movement. In the colleges it has had recognition since the beginning of the nineteenth century. Indeed one college, the College of New Jersey (Princeton), had made definite provision for instruction in chemistry to undergraduates as early as 1795.[1] The growth of this subject in high schools and colleges has closely paralleled the development of the science itself.

Chemistry in American Secondary Schools

The academy was the first American secondary school to provide instruction in chemistry. This type of school came into being during the last half of the eighteenth century and the purpose of its promoters was to develop an institution in which adolescent students might acquire a liberal and practical education. In the early days of the academy much emphasis was placed upon the importance of training in agriculture and mechanics. The work of Davy and others on the applications of chemistry to agriculture and the many references to the practical value of chemistry in the trades and industries helped in no small way to secure for this subject a place in the "practical" course of study of the academy. As early as 1830 it had come to occupy a position of some prominence in the course of study of this institution.[2] Although the method of instruction was, for the most part, through the study of textbooks, the importance of illustrating the work by use of apparatus for demonstrations was recognized. Evidence of this is seen in advertising materials which set forth the claims of some of these schools. In an ad-

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[1] Maclean, John, "History of the College of New Jersey," **2**, pp 8–9.

[2] Powers, S R., "A History of the Teaching of Chemistry in the Secondary Schools of the United States Previous to 1850," University of Minnesota, *Research Publication*, **1920**, pp 16–17.

vertisement of the Oxford Female Academy which appeared in the Raleigh (North Carolina) Register of March 23, 1827, it is stated:

> Since the commencement of the session we have received a chemical and philosophical apparatus and now each recitation in chemistry, philosophy, and astronomy is accompanied with a lecture and experiments illustrating the principles of these sciences.[1]

That chemistry occupied a larger place in secondary education of this period than available records show is indicated by the number of textbooks which had been prepared for use in secondary schools. As many as eight books, written or revised by Americans, were available for use in the Academy by 1833.[2]

The first public high school in the United States, the English Classical School, now the English High School, was founded in Boston in 1821, and the second was the High School for Girls, Boston, which was founded in 1826.[3] In the girls' school it was provided that the course of study "should include as much chemistry as would be useful in domestic economy."[4] Throughout the cities of Massachusetts instruction in this subject was given at an early date. In 1857 Massachusetts passed a law which required that:

> Every town may and every town containing 500 families * * * shall maintain a school kept by a master * * * who * * * shall give instruction in * * * geometry, natural philosophy, chemistry, botany and * * * .[5]

Inglis reports that in three Massachusetts towns the number of students enrolled in chemistry in 1860 was 50.7 per cent of the number enrolled in algebra, and that during this same year, of fifty-five towns of five hundred families or over, fifty-two included chemistry in their course of study.[6]

In the high schools of Ohio the sciences received early recognition. The first report of the state commissioner of education was published in 1854. This and subsequent reports show that instruction in chemistry was offered to a considerable number of students. In 1855–1856 the number of students engaged in the study of this subject was 55 per cent of the number engaged in the study of geometry.

Chemistry was recognized in most of the large cities throughout the country as an important subject for secondary education at least as early as the decade of 1860–1870. Even earlier than

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[1] Coon, Charles L., "North Carolina Schools and Academies, 1790–1840. A Documentary History," pp 156–57.

[2] Powers, S R , "A History of the Teaching of Chemistry in the Secondary Schools of the United States Prior to 1850," pp 19–20.

[3] Brown, E. E , in Edmonds' "History of Franklin High School of Philadelphia," p. 29

[4] "Boston High School for Girls " *Am J Education*, **1,** 99 (1826).

[5] Mass Bd. Education, 24th Ann. Rpt , **1861**, p 91

[6] Inglis, A., "Rise of High Schools in Massachusetts," Columbia University, Teachers College, **1911**, pp. 84 and 90.

this it had come to occupy a place of importance in the course of instruction in certain cities and in some of these rather liberal provision had been made for laboratory instruction. Williams says in his report on the "Teaching of Chemistry in Schools, 1876–1901:"

> One of the earliest, perhaps the first, to adopt the new idea (laboratory) was the Girls High and Normal School, of Boston, about 1865. It was followed by the Cambridge, Massachusetts, High School in 1866, and the English High of Boston in 1871.[1]

There is evidence that laboratory instruction in chemistry was given prior to this in some midwestern high schools. The Central High School of Philadelphia entered a new building in 1854 in which there was a room set apart for a laboratory for chemistry and natural philosophy.[2] However, this room was not equipped for individual laboratory work until some years later. Chemistry was included in the first program of studies constructed for high schools in Chicago.[3] The first high school building erected in St. Louis (1854)[4] contained a chemical laboratory equipped for student use.

It is clear that the high school in St. Louis and probably some in other midwestern cities were equipped with laboratories at an earlier date than 1865. A survey, in 1867, by Henry Barnard, shows that of thirty large high schools distributed over the United States all gave instruction in algebra, geometry, and natural philosophy, and twenty-six gave instruction in chemistry.[5]

By 1860 the high school was an established educational institution. It should be recalled that the academy came into being as an institution which should furnish a more liberal and practical education than the Latin-grammar school, which was its predecessor. By 1860 it was evident that the academy could not survive and that an adequate system of popular secondary education could be developed only through state-controlled schools.

Throughout the period of their existence the high schools have given a place to the sciences. Stout has assembled high-school courses of study which were prepared between 1860 and 1900 and has computed from these, by five-year periods, the average amount of time allowed for instruction in each group of subjects. He has found that the amount of time allowed for

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[1] Williams, R P , "Teaching of Chemistry in Schools, 1876–1901," *J. Am Chem Soc* , Supplement (Twenty-fifth Anniversary of the American Chemical Society), p. 128 (1902)

[2] "History of Central High School, Philadelphia," p 142, and Hart, J S , "Description of a Public School in Philadelphia," Barnard's *Am J. Education*, **1**, 93 (1856)

[3] Wells, W H., "Public High School in Chicago," Barnard's *Am. J. Education*, **3**, 531 (1857)

[4] Tice, J H., "First Annual Report of the St. Louis Schools," Barnard's *Am J Education*, **1**, 353 (1856).

[5] Barnard's *Am J Education*, **19**, 463 (1869).

science was equal to or greater than that allowed for mathematics, and that Latin was the only subject or related group of subjects which was allowed more time.[1] All the courses examined for 1860–1865 showed an offering of physics (or natural philosophy). Eighty-five per cent offered chemistry. Throughout the period 1860–1900 physics was recognized by 100 per cent of the courses examined. Chemistry was included in from 60 to 90 per cent of the courses of each five-year period.

The extent to which chemistry was recognized as a subject of study in high schools in 1878 is revealed from the survey conducted during this year by the United States Bureau of Education.[2] Of one hundred and seventy-six public high schools, one hundred and fifty-four offered some instruction in chemistry. Of these, fifty-six made provision for some individual laboratory work and seventy-three illustrated the work with demonstrations which were prepared and presented by the teacher. The remainder of these schools, forty-seven in number, made no mention of laboratory work by the pupils or of demonstrations by the teacher. Of the one hundred and seventy-six public high schools included in the report, thirty-nine sent descriptions of their work which indicated that they had developed, with considerable care and thoroughness, the laboratory method of study and teaching.[3]

In the light of these reports it appears that chemistry has occupied nearly as large a place in the program of studies of the early high schools as it does today. Most of the "standard" schools have always provided a place for it. As already suggested, in the earlier period there were great variations in the kind of recognition which was given. In sixty-eight of the public high schools in the list of the Bureau of Education (1880), the course was given for but one-half year or less, and in many of these the total number of exercises, including recitations per week, was less than five. In laboratory equipment the variation was from none up to apparatus which, for chemistry and physics combined, had cost from three to four thousand dollars.

The past fifty years have not witnessed the extension of instruction in chemistry in a considerably larger proportion of the public schools. There were, however, two important developments during this period: (1) It has witnessed a standardization of content and methods; and (2), it has contributed a

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[1] Stout, J. E., "The Development of High-School Curricula in the North Central States from 1860–1918," Supplementary Educational Monographs (University of Chicago), Vol. III, No. 3, 1921, pp. 90–91.

[2] Bur. Education, *Circ Information* 6, pp 170–74 (1880).

[3] *Ibid*., pp. 20–22

definition of objectives and the beginnings of a critical evaluation of these objectives by the application of scientific methods to education. These developments relate to instruction in college chemistry, as well as to high-school chemistry, and we shall return to them after taking an over-view of the history of chemistry in colleges.

Chemistry in American Colleges

The foundation of modern chemistry is in the work of Black, Cavendish, Lavoisier, Priestley, and others who worked during the latter part of the eighteenth and the early part of the nineteenth centuries. Before Priestley's death in 1804, Princeton, Columbia, and Harvard had made chemistry a required study for students who were candidates for the baccalaureate. However, it was many years before it was given a place of prominence in the curriculum. As late as 1875 the provision which had been made for chemistry in most of the colleges was quite meager. The progress since that time may be illustrated by reference to the offering for different years in representative institutions.

At the College of New Jersey (Princeton) in 1871–1872 chemistry was a required subject only during the senior year and this constituted the sole offering. Professor Schanck gave lectures in (1) General Chemistry and (2) Applied and Organic Chemistry. He also gave lectures in (1) Zoölogy and (2) Anatomy of Physiology.[1]

There were but few changes in the titles of the courses offered in this college for several years. It was stated in 1881 that:

> Students in the academic department attend a required course in applied chemistry throughout the entire senior year. The aim is to give a full course of instruction in general chemistry occupying two hours in the class room each week and in this attempt is made to give quite fully the leading principles and facts of general chemistry, enforced by carefully prepared experimental illustrations. Free use is made of lantern projections, and recitations and written examinations are required. The additional parallel and elective course embracing the leading applications of chemistry in the arts of life, also illustrated fully, occupies one additional hour each week.
>
> Laboratory chemistry constitutes an elective study in the senior year. The class attend lectures with occasional recitations and also work in the laboratory The course requires about four hours per week; three hours being generally devoted to laboratory work and one hour to lectures and recitations.[2]

There was an offering of a "general science course" in which chemistry was taken during the sophomore year. In 1880–1881 there were two professors of chemistry and one assistant at Princeton. In 1890–1891 general chemistry was required during the first semester of the sophomore year and an elective course in general chemistry was offered for the first semester of the

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[1] Calendar of the College of New Jersey, 1871–72, p. 41.

[2] Princeton University Catalogue, 1882–84, p. 59.

junior year. A laboratory course consisting of qualitative analysis, organic compounds, and special examination of water, milk, etc., was elective during the senior year. In 1900–1901 general chemistry was a required subject in the second half of the sophomore year and an elective course, including organic chemistry, was offered during the senior year. The work had been differentiated to the extent of including eight additional elective courses. In 1905–1906 the work of the Department of Chemistry was given under "School of Science" and a course was offered for the training of chemical engineers. Nineteen distinct courses were listed, six being graduate courses. During this year there were five professors of chemistry and two assistants. In 1910, Princeton employed four professors, two instructors, and twelve assistants.

The following tabular statement shows the progress of the development of chemistry at Harvard University.

Courses in Chemistry Offered at Harvard in 1875–76, 1895–96, 1915–16, with Number of Students in Each

	NUMBER OF STUDENTS		
TITLE OF COURSE	1875–76	1895–96	1915–16
Elementary chemistry	251	268	221
Inorganic chemistry	..	..	129
Descriptive chemistry with laboratory practice	53	..	.
Advanced inorganic chemistry	.	.	88
Quantitative analysis	40	94	68
Mineralogy	2		.
Quantitative analysis	9	24	53
Organic chemistry	7	19	159
Advanced quantitative analysis	..	9	20
Gas analysis		11	20
Experimental chemistry	.	75	90
History of chemistry and chemical philosophy		9	.
Research courses (differentiated)		12	34
Physical chemistry		..	38
Experimental organic chemistry		.	55
Fire assaying			3
Metallurgical chemistry			3
Carbon compounds			55
Biological chemistry			36
Experimental biological chemistry		..	7
Industrial chemistry			56
Technical analysis	.		7
Photochemistry	.	.	19
Electrochemistry	.		17
Experimental electrochemistry	.	.	4
Chemical equilibrium	..	..	3
General reactions of organic chemistry	..	..	15
Structural organic chemistry	.	..	12
Total number of courses offered	6	9	25

In 1885 there were three professors of chemistry at Harvard; in 1895 there were four; and in 1915 there were nine professors, two instructors, and twenty-four assistants.

Elementary chemistry at Harvard in 1875–1876 was given to freshmen and consisted of one "exercise" each week for twenty-four weeks. During this year there was an appropriation of $800 for the chemistry laboratory and a special appropriation of $703.65 to fit up a laboratory of organic chemistry. In 1895–1896 research courses were offered in inorganic, organic, and physical chemistry, and twelve students enrolled in these courses. By 1900 the number of research students had increased to seventeen. The further gain in registration for research reflects the influence of German universities and constitutes one of the most significant developments of this period. In 1905 there were nineteen students enrolled in research courses, in 1915 thirty-four, and in 1920 thirty-seven.

The reports of Professor Chandler to the president of Columbia University show some of the difficulties with which he was forced to cope and reveal a situation which is quite in contrast with the one which prevails in this university today. In 1881 he wrote:

> I have the honor to report that in the academic department of the college I have met the sophomores once a week and have gone over the non-metallic elements. The holidays and monthly examinations reduce the number of exercises to such a degree that it is not possible to go over a great deal of ground. I think it would be a great improvement to double, if possible, the number of exercises, and allow the sophomores to come to me twice a week. I should then be able to give them a fair initiation into the field of chemistry
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> The seniors, or rather an elective section of them numbering twenty-nine, have attended three times a week with the second section of the School of Mines. The first term was devoted to inorganic chemistry, the second term to organic chemistry.[1]

In 1884 Professor Chandler reported:

> There has been one graduate student attending instruction in chemistry but for several reasons he has not been able to accomplish a great deal. Under a rule of the Board of Trustees he is not permitted to enter the analytical laboratories of the school—the only laboratory in which he can work under the present rules is the organic laboratory.[2]

Somewhat more attention was given to the study of chemistry in some of the midwestern universities than in the universities of the East. This may have been due in part to a greater willingness to break with the tradition which emphasized so strongly the importance of the classics. Furthermore, the agricultural states fostered the development of agricultural and mechanical colleges in connection with their state universities and chemistry was an essential subject in these institutions. As early as 1880–1881 chemistry had been differentiated into thirteen courses at the University of Michigan. The title of one of these was

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[1] Annual Report of the President of Columbia University to the Board of Trustees, 1881, p. 113.

[2] *Ibid.*, 1884, p 70

"Original Investigations." This suggests that the major purpose of the course was the promotion of research.

The past fifty years have witnessed an enormous expansion of college work in chemistry. As we have seen, chemistry was assigned a place in the college course of study long before the opening of this period but it was a very inconspicuous one. Princeton has been recognized as the first American college (1795) to give lectures in chemistry to liberal arts students, but in 1871 the entire offering was given by one man who divided his time with other subjects. In 1800 the trustees of Columbia College determined that the study of the "chemical branch of physics" should precede the conferring of the degree of bachelor of arts, but in 1884 they had only one graduate student in chemistry and were poorly equipped to care for him. The rapid growth since 1875 may be measured by the increase in the number of differentiated chemistry courses; by the increase in the number of professors on the college faculty; and by the increased attention to graduate study and research.

An important accompaniment to the progress of chemistry has been the development of its application to mechanical and industrial pursuits. Chemistry is part of the training for all fields of industrial engineering. It is considered an essential study for the preparation of pharmacists, physicians, dentists, nurses, agriculturists, and research workers in all fields of science. The phenomenal growth of chemistry in colleges is unparalleled by any other subject.

Objectives of Instruction in Chemistry in Colleges

Two practical objectives guided the growth of chemistry as a subject of instruction in colleges. One of these was to teach chemistry as related to the manufacturing industries and the other its relation to agriculture. The possibility of extensive application of chemistry to industry was recognized as early as 1815, when it was said that chemistry was

> an important aid to the study of mineralogy, pharmacy, electricity, cooking, metallurgy and in various manufacturing industries, especially glass, leather, soap, paint, glue, starch, etc. In fact it would be an easy task to continue almost indefinitely the list of arts whose processes, if they admit of explanation at all, must be explained upon the principles of chemical philosophy.[1]

However, at as late a date as 1870 when the value of manufactured chemical products in France was 250 million dollars, the total value of American chemical products, including fertilizers, was but $25,217,000.[2] The total value of the products from chemical

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[1] An unsigned essay on "The Classification, Mutual Relations and Various Uses of Physical Sciences," *Analectic Magazine*, 6, 145 (1861).

[2] Bolles, Albert S., "Industrial History of the United States," 1879, p. 489.

industry in 1923 was nearly six billion dollars. During the same year chemical industry employed 384,493 wage earners, paid \$501,205,000 as wages, and used 2,739,519 horsepower.[1] The individuals who have developed this great industry for the most part have had their training in the technical schools. The development of industrial chemistry has been a leading objective of education in chemistry, and the present status of chemistry in industry is abundant evidence of successful accomplishment.

The importance of chemistry to agriculture was also recognized at an early date. In 1811, the Philadelphia Society for Promoting Agriculture recognized the possible application of chemistry to the maintenance of soil fertility. In its "Memoirs" were articles on the use of lime, gypsum, leached ashes, and salt as material for fertilizing, and it was lamented that there was not more exact knowledge of these substances.[2] Notwithstanding the frequent reference to the importance of applying chemistry to agriculture, the large developments have come during comparatively recent years. There are, in fact, many indications that this field is due for rather rapid advancement in the immediate future.

A third objective has been the promotion of research. As already indicated, there was but little research in chemistry in American universities of fifty years ago. The instruction in the School of Arts of Columbia College was not planned to promote research in 1875, nor for several years later. It was said in 1878 that in the School of Mines,

> this course of study is designed to train analysts and technologists, rather than purely scientific investigators. A considerable amount of original research work has, however, been done by the graduates of the course and a small pamphlet catalog of their publications has been prepared.[3]

At Princeton in 1878 "Postgraduate courses are offered" but there was little or nothing in the nature of research.[4] At Yale, during this same year, instruction in chemistry in the undergraduate academic department was given by one professor in the first third of the junior year, but there was no laboratory practice. Postgraduate courses in theoretical and analytical chemistry, agricultural chemistry, and metallurgy and assaying were given in the department of philosophy and the arts. In the Sheffield Scientific School "a good deal of original research

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[1] "World Almanac and Book of Facts for 1925," p 330.

[2] "Memoirs of the Philadelphia Society for Promoting Agriculture, Containing Communications on Various Subjects in Husbandry and Rural Affairs," 1811. Reviewed in *American Review*, **2**, 78–101.

[3] Bur Education, *Circ. Information* **6**, pp. 65–68 (1880).

[4] *Ibid.*, pp. 75–76.

work is done by teachers and advanced students and a very large number of scientific memoirs have been published from the school."[1]

At Harvard, "In the laboratories advanced students are directed by the professors in whatever special studies or investigations they may desire to undertake."[2]

These references are sufficient to illustrate the meager recognition which was given to research in chemistry fifty years ago. Its importance was recognized, however, and effort was directed towards its stimulation. A measure of the success with which this objective has been accomplished may be had in terms of the enormous accumulations of reports of research; in terms of the influence which the results from research have had on present conditions of living; and in terms of the number of individuals now employed as research workers.

The materialistic contribution of chemical education has been most evident, but its cultural value has been none the less significant. The development of this science came at a time when the culture of the people was greatly influenced by superstition and mysticism. The development of chemistry and other sciences was accompanied by an accumulation of factual information about many phenomena which, for all time, had been looked upon as beyond human comprehension. The research scientists discover and rationalize the causes which lie back of effects. The educational outcome from instruction which shows relation of cause and effect, relative to phenomena which had been looked upon as mysterious, leads to the belief that all phenomena are results from definite causes and that all unexplained events may be rationalized if the facts relative to them are discovered. This aspect of the scientific method has, more than any other, influenced the thinking of educated individuals who are not specialists in science. The development of science and the frustration of superstition have paralleled since the middle of the eighteenth century. A general dissemination of this attribute of the "scientific attitude of mind" has been an achievement of the past fifty years. But much remains to be done.

It will be seen that the major accomplishments of college education in chemistry have been: (1) the development of industrial and agricultural applications; (2) the development of research; and (3) the general diffusion of the method and attitude of mind of the scientist.

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[1] Bur. Education *Circ Information* 6, pp 57–59 (1880).

[2] *Ibid.*, p. 48.

Objectives of Instruction in Chemistry in Secondary Schools

It has already been shown that the past half-century has not witnessed any considerable extension of instruction in chemistry in high schools. The percentage of the four-year high schools of the United States offering this subject has remained fairly constant since 1876. This period has, however, witnessed the standardization of content and, in considerable measure, the method of instruction. This has resulted: (1) from the work of influential committees; (2) from Smith and Hall's textbook;[1] (3) from the influence of texts written by college teachers and used in high schools; and (4) from the transplanting by teachers of the content and method which they had learned in college to the high school. It will be profitable to make some examination of each of these standardizing agencies and, if possible, to suggest some evaluation of the objectives which they have set for accomplishment in secondary schools.

Fifty years ago the course in high-school chemistry was poorly defined, and there was wide divergence in practices relating to methods of teaching. The recognition of the subject as one suitable for a college entrance unit has, more than anything else, effected a standardization of content and of method.

An analysis of the entrance requirements of forty-four colleges in 1879 showed that only three (Iowa State University, California State University, and Boston University) recognized chemistry.[2] This issue was brought to a focus by the action of Harvard College in 1888 when, for the first time, it included chemistry among the subjects that might be offered for admission. Professor Cooke issued this same year his "Laboratory Practice," which defined chemistry as the true educational equivalent of the other and older preparatory school subjects. This book was the first in this country which attempted to standardize the laboratory work in high-school chemistry, and the results from its use were in

> marked contrast to the miscellaneous experimentation with chemical substances, and the dabbling in qualitative analysis which had hitherto been in use and had afforded so little support to the classroom work on the principles of science [3]

It was at this time that the advocates of a number of newer studies were clamoring for recognition as college-entrance sub-

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[1] Smith, Alexander, and Hall, Edwin H, "The Teaching of Chemistry and Physics in the Secondary School," 1902, Longmans, Green & Co, N Y.

[2] Nightingale, A F, "A Hand Book of Requirements for Admission to the Colleges of the United States," 1879, pp 10–25.

[3] Smith, Alexander, and Hall, Edwin H, "The Teaching of Chemistry and Physics in the Secondary School," 1902, p 19, Longmans, Green & Co, N Y.

jects and that the more progressive of the college administrators were recognizing the need for a more liberal course of high-school instruction than was afforded by the study of the classical languages and mathematics. An effort to promote these two progressive movements found expression in the work of the Committee of Ten of the National Educational Association.

The report of the Committee of Ten has probably had the most far-reaching effects on secondary education of any document that has ever been printed. In his letter of transmittal to Hoke Smith, Secretary of the Interior, W. T. Harris, commissioner of education, said:

> It has been agreed on all hands that the most defective part of the education in this country is that of the secondary schools. There is a wide divergence in the course of study, and the difference of opinion regarding what constitutes a secondary education works injury not only to the elementary schools by setting up an uncertain standard of admission but also through a want of proper requirements for graduation prevents in thousands of cases the continuance of the course of education of youths in colleges and universities. The recommendations of this report will draw the attention of great numbers of teachers to the question of educational values and this will lead to a better understanding of what the pupil should study to gain the most from his work in school. In this respect I consider this the most important education document ever published in this country.[1]

The committee was appointed in July, 1892, with President Charles W. Eliot of Harvard University as chairman. The members met at Columiba University on November 9 and decided to organize conferences on nine subjects or groups of subjects. One of the groups included physics, astronomy, and chemistry. Ten members were appointed to each of the conferences and each conference was requested to submit its report to the chairman of the main committee by April 1, 1893. The complete reports were submitted to the Department of the Interior for publication in December, 1893.

The conference on physics, chemistry, and astronomy met on December 28, 1892, at the University of Chicago. Prof. Ira Remsen of Johns Hopkins University was elected chairman. The recommendations of the conference affecting chemistry were:

(1) That the study of chemistry should precede the study of physics and that physics be pursued the last year of the high-school course.

(2) That at least 200 hours be given to the study of chemistry in the high school.

(3) That both physics and chemistry be required for admission to college.

(4) That there should be no difference in the treatment of chemistry for those going to college or scientific school and for those going to neither.

(5) That chemistry be taught by a combination of laboratory, textbook and thorough didactic instruction carried on conjointly, and that at least one-half of the time devoted to this subject be given to laboratory work.

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[1] Bur. Education, Report of the Committee on Secondary School Subjects, 1893, p ii.

(6) That careful notebook record of the laboratory work be kept by the student at the time of the experiment.

(7) That the laboratory record form part of the test for admission to college and that the examination for admission be both experimental and either oral or written.

(8) In the opinion of the conference admission to college should be by certificate from approved schools.

(9) In the opinion of the conference it is better to study the subject as well as possible during the whole year than to study two or more superficially during the same time.

(10) It should not be the aim of the student to make a so-called rediscovery of the laws [1]

A committee of two was appointed to make out, subject to the approval of the conference, a list of fifty experiments in physics and one hundred experiments in chemistry. The report of this subcommittee is appended to the report of the conference. At this meeting it was

Resolved, That in the opinion of this joint conference at least one quarter of the time of the high-school course should be devoted to nature studies and that this amount of work should be required for admission to college.

One member of the conference opposed placing chemistry before physics in the course of study but with this exception the ten members were in complete agreement.

The report of the Committee of Ten urged the recognition of a wider range of subjects for college entrance. The high school was "the people's college" and must offer a rich and varied course of study. The classical languages and mathematics had been recognized by the colleges as the studies most acceptable for college entrance and students who had pursued other subjects, particularly the natural sciences, were frequently embarrassed when they applied for entrance.

In 1895 Prof. William Corey Jones, of the University of California, read a paper before the Department of Secondary Education of the National Education Association on the subject, "What Action Ought to Be Taken by Universities and Secondary Schools to Promote the Introduction of the Programs Recommended by the Committee of Ten?" Discussion of this paper led to the appointment at this session of the Committee on College Entrance Requirements. The final report of this committee was issued in 1899.

The report of the chairman to the meeting of the association in 1896 made special mention of the sciences. He said:

The sciences as they are beginning to be taught in our best schools add to the wealth of mind as well as the stock of facts and the colleges must recognize them as full equivalents for other work which they have hitherto demanded to the exclusion of science.

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[1] Bur Education Report of the Committee on Secondary School Subjects, 1893, pp 116–21

In their preliminary report of this year[1] the committee presented an analysis of the entrance requirements of fifty-six of the "most important institutions." This analysis shows that twenty-four of the fifty-six institutions required or recognized chemistry as a college entrance subject. Three institutions required physics or chemistry; four required physics and chemistry; and thirteen required physics and chemistry and "some other good natural science subject."[2] In their summation of the requirements in natural science, the committee noted that "the average requirement is very low, incoherent, and illogical."

In its "Plan of Work for 1896–1897" it was recommended that the committee should invite the active coöperation of specialists in the various subjects and that special attention should be given to what constitutes a year's work in each subject.[3] This recommendation prevailed. Alexander Smith, then of the University of Chicago, was made chairman of the Committee on Chemistry. The divisions of his committee report were: (1) value and place of chemistry; (2) outline of a one-year course; (3) methods of teaching, with recommendations for laboratory, classroom, and library work; (4) subject matter; and (5) equipment.[4] This committee incorporated many of the recommendations of the Committee of Ten, including the statement that at least 200 hours be allowed for the one-year course and that about one-half the time, in two-hour periods, should be spent in the laboratory. They took exception to the recommendation relating to sequence by placing chemistry in the fourth year of the high school and physics in the third.

Professor Smith's treatise on "The Teaching of Chemistry and Physics in the Secondary School"[5] appeared in 1902, three years following the issuance of the Report of the Committee on College Entrance Requirements. It met a real need in that it furnished a practical guide for the accomplishment of the committee's recommendations. Professor Smith's book gave a definition of the place of chemistry in the high-school curriculum, and it contained chapters on Instruction in the Laboratory; Instruction in the Classroom; Some Constituents of the Course; The Laboratory, Equipment, and Illustrative Material; and The Teacher, His Preparation and Development.

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[1] "Preliminary Report of the Committee on College Entrance Requirements," *School Review*, **4**, 341–460 (June, 1896)

[2] *Ibid*., p 453.

[3] National Education Association, Report of Committee on College Entrance Requirements p 9 (July, 1899)

[4] *Ibid*., pp 165–71

[5] Smith, Alexander, and Hall, Edwin H., "Teaching of Chemistry and Physics in the Secondary School," **1902**, Longmans, Green & Co., N Y

No factors affecting education in high-school chemistry have been so potent as those associated with the standardization of the course for college entrance. The past fifty years have witnessed progress from almost no recognition to complete recognition by practically all colleges and universities.

The content and methods of high-school chemistry have been determined in large measure by the textbooks available. Through these, college professors of chemistry have until quite recently enjoyed almost complete domination. This domination has been wholesome and necessary through the formative period of secondary education. Those equipped in training and scholarship to write books were for the most part in college positions, although there have always been some notable exceptions. During the past decade some of the most popular books have come from the pen of high-school teachers, but thus far none have broken with the tradition established by the college authors.

The Outlook for Chemical Education

The past fifty years have witnessed the establishment of practices and the extension of instruction until today chemistry is, in some manner, affecting the lives of thousands of students. It is now time to make some evaluation and some refinement of these practices.

The past quarter-century has seen notable contributions to the methods of educational investigation and study, and these have come in large part as a result of transfer of the method of work evolved by scientific workers in the fields of the biological and physical sciences to this field. Educational workers, like chemists, are no longer content with philosophy or theory which has no factual foundation. Acceptance of educational theory and philosophy is now conditioned upon factual support. Opinionated committee recommendations are no longer adequate. The future of chemical education is, in large measure, dependent upon the application of the scientific method to the study of its problems.

It has already been shown that the reports of the Committee of Ten (1893) and the Committee on College Entrance Requirements (1899) have greatly influenced present practices. Their recommendations relating to content and method have been accepted because they came from experts who were presumably most competent to advise concerning these matters. The future will see the scientific method used in testing and evaluating the practices which have evolved from the deliberations of these committees. In fact, this testing and evaluating is now in progress.

The Committee on College Entrance Requirements outlined a high-school course of study which was similar but presumably simpler than the freshman college course. A recent study reports a quantitative analysis of the content of instruction in the high school and in the first-year college course.[1] This analysis shows that there is almost no part of the high-school course which is not repeated in the college course.

Facts relative to some of the committees' recommendations of methods have recently been reported. One study reports an evaluation of different methods of laboratory procedure and shows that, for the accomplishment of certain objectives, the teacher-demonstration method is equally or possibly more effective than the individual method of laboratory work.[2]

A measure of the relative values of different methods for recording laboratory notes has been reported. The study reports the results of experimental teaching in which three methods of recording were used. These methods were evaluated by administering tests of achievements to the students after the experiment.[3] Another study compares the achievement of high-school students in three high schools with that of freshmen students in three colleges on tests prepared from the first division of the "Syllabus for College Freshmen" prepared by the Committee on Chemical Education of the AMERICAN CHEMICAL SOCIETY.[4] This study shows that the differences in achievement on these tests by students in good high schools and in good colleges is relatively small. Another report gives an analysis of the errors which pupils make after instruction.[5] The author of this study contends that it reveals the points at which more intensive instruction must compensate deficiencies in learning ability. A significant trend is illustrated by a report of an analysis of the needs for instruction in chemistry of certain vocational groups and an outline of a course of study to meet this need.[6]

[1] Koos, L. V., "Overlapping of High School and College Chemistry," The Junior College, Ch XXXIII 1925.

[2] Carpenter, W. W., "Certain Phases of the Administration of High-School Chemistry," Columbia University, Teachers College, *Contributions to Education* **191** (1926)

[3] Stubbs, M. F., "An Experimental Study of Methods for Recording Laboratory Notes in High-School Chemistry," *J. Chem. Education*, **3**, 296–300 (1926).

[4] Mabee, Fred C., "A Test of Achievement in College Chemistry and Results Obtained by Its Use with Both High-School and College Classes," *J. Chem Education*, **3**, 70–76 (1926).

[5] Bennet, J. C., "A Study of Pupil Errors in Chemistry," *J Chem. Education*, **2**, 760–69 (1925)

[6] Beery, Pauline, "A Practical Course in Household Chemistry," *J. Educational Research*, **5**, 125–34.

These reports are sufficient to illustrate present trends in chemical education. Their significance lies in the fact that they illustrate some of the ways in which the methods of science are applied to educational problems. In education, as in so-called pure science, the development of hypotheses and theories and the formulation of more intelligent philosophy follow upon the accumulation of factual material, such as is reported in these studies. An important problem, and one about which but little is definitely known, is what should constitute the course in chemistry for students who are not preparing for specialization? The history of the development of the high-school and college-freshman courses shows that their present content has been selected in an effort to train technical chemists and research workers. The technician is a creator of chemical products and the investigator is a revealer of truth. The major objective of a liberal education in chemistry is to teach an interpretation and appreciation of the truths of chemistry and, in some measure, to train in intelligent usage of chemical products. There is need for a factual statement of what chemical truths are of most importance to a program of liberal education and for a statement of what is needed most in the way of training for intelligent consumption. A course which is designed for students who are not preparing for specialization should embody this content. Up to this time it has been assumed that the same chemistry course was sufficient for all. It is now time to question whether the course which is best for vocational training is also best for liberal training.

Closely related to the problem of developing a course for liberal training in chemistry is the problem of providing a proper differentiation of courses to meet the needs of various vocational groups. There is an evident feeling of doubt that the present course in chemistry for dentists, for example, is for them either vocational or cultural in the best sense. The vocational values of chemistry for dentists (or for medical students, nurses, or civil engineers) have not been carefully defined. Attention to this problem will surely effect an economy of time to students and financial economy in colleges.

Some other important problems for immediate study are:

What should constitute the training in chemistry for college preparation, and how should the college preparatory course be correlated with the college course?

What are the values which should come from laboratory work in training for a liberal education?

Is there support for the present emphasis on laboratory notebook work?

Is chemistry an appropriate subject for study in small high schools in which laboratory equipment is necessarily meager?

How much and what kind of laboratory equipment is necessary for successful high-school work?

What are the fundamental concepts and generalization of chemistry? Of what use are these fundamentals?

How may the method and content of chemistry be modified so as to raise effectively the standards of accomplishment in useful learning?

How can the high-school and liberal arts college course be taught so as to accomplish more effectively training in the methods of the scientists?

The important developments of the immediate future will come from application of the scientific method of study to these and similar problems.

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FIFTY-FIRST YEAR

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- *Annual Report on Atomic Weights:* (Est. 1897.) G. P. Baxter, Coolidge Memorial Laboratory, Cambridge, Mass.

Chemical Education: (Est. 1923.) Neil E. Gordon, University of Maryland, College Park, Md., *Chairman*, B. S. Hopkins, D. B. Keyes, L. W. Mattern, L. C. Newell, R. E. Rose, W. Segerblom, T. G. Thomson, R. E. Swain, F. B. Wade, F W. Willard.

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Hazardous Chemicals and Explosives (To Coöperate with National Fire Protection Association's, Committee on the same subject): (Est. 1923.) C. E. Munroe, Forest Glen, Md., *Chairman*, H. LeB. Gray, A. H. Nuckolls, J. A. Rafferty, F. C. Zeisberg.

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Journal of Physical Chemistry. A. C. S. Representatives on Editorial Board: (Est. 1924.) A. L. Day, G. A. Hulett, Irving Langmuir, W. Lash Miller.

Membership. (Est. 1876.) W. D. Bigelow, National Canners' Assoc., 1739 H St., N. W., Washington, D. C., *Chairman*, F. G. Cottrell, Chas. L. Parsons.

Metric System: To coöperate with the American Metric Assn., World Trade Club, London and Manchester Metric Association: (Est. 1915.) E. C. Bingham, Lafayette College, Easton, Pa., *Chairman*, Wm. Blum, W. F. Coover, E. W. Magruder, W. A. Noyes, Wm. Segerblom, R. E. Swain,

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Nomenclature, Spelling and Pronunciation: (Est. 1894.) E. J. Crane, Editor, *Chemical Abstracts*, Ohio State Univ., Columbus, Ohio, *Chairman*, Board of Editors of the *Journal of the American Chemical Society*, Editor of *Industrial and Engineering Chemistry*, and A. M. Patterson.

Occupational Diseases in Chemical Trades: (Est. 1913.) L. W. Fetzer, 1428 Washington Ave. Dallas, Tex., *Chairman*, Geo. P. Adamson, Edward Bartow, H. K. Benson, M. L. Crossley, H. H Dow, F. R. Eldred, Elias Elvove, E. K. Strachan, A. H. White.

Paper: (Est. 1908.) F. P. Veitch, Bureau of Chemistry, Washington, D. C.

Patent and Related Legislation: (Est. 1899.) Henry Howard, Grasselli Chemical Company, Cleveland, Ohio, *Chairman*, E. A. Hill, H. C. Parmelee, W. A. Schmidt, C. P. Townsend.

Preparation and Publication of a List of Ring Systems Used in Organic Chemistry. Joint with the National Research Council: (Est. 1922.) A. M. Patterson, Xenia, O., *Chairman*, M. T. Bogert, J. W. Kinsman, W. A. Noyes, R. R. Renshaw.

Prize Essays: H. E. Howe, Mills Bldg., Washington, D. C., *Chairman*, W. D. Bancroft, Chas. H. Herty, Paul Smith.

Revision of Methods of Coal Sampling and Analysis (Joint with the Society for Testing Materials): (Est. 1912.) S. W. Parr, Urbana, Ill., *Chairman*, A. C. Fieldner, A. H. White.

Standard Apparatus: (Est. 1917.) W. D. Collins, U. S. Geological Survey, Washington, D. C., *Chairman*, W. A. Boughton, H. E. Howe, F. W. Smither, G. C. Spencer, H. H. Willard.

Standard Methods for the Examination of Water and Sewage to Coöperate with Committee of American Public Health Association: (Est. 1920.) Arthur M. Buswell, Univ. of Ill., Urbana, Ill., *Chairman*, W. D. Collins, F. W. Mohlman, E. B. Phelps.

Standardization of Biological Stains: (Est. 1924.) A. C. S. Representative, Joseph A. Ambler, Peil Hotel, St. Petersburg, Fla., *Chairman*.

Standardized Methods for Vitamin Research: (Est. 1921.) H. C. Sherman, Columbia University, New York City, *Chairman*, A. D. Emmett, A. F. Hess, E. V. McCollum, L. B. Mendel.

Supervision of Chemical Engineering Catalog: (Est. 1915.) Wm. Hoskins, Room 2009, 111 W. Monroe St., Chicago, Ill.

Supervisory on Standard Methods of Analysis: (Est. 1910.) H. H. Willard, University of Michigan, Ann Arbor, Mich., *Chairman*, A. C. Langmuir, G. E. F. Lundell, W. W. Skinner, G. C. Stone.

Issued with the July Number, 1926

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A STUDY OF THE OXIDES OF POTASSIUM AND SODIUM

By Charles A. Kraus and Earle F. Whyte

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Introduction

Although numerous investigators have studied the oxides of potassium and sodium, our knowledge of these oxides is still far from complete. Harcourt[1] showed that the highest product of direct oxidation of potassium is K_2O_4. Holt and Sims[2] confirmed the results of Harcourt. They found indications of the existence of the dioxide K_2O_2 and of the trioxide K_2O_3, the latter being obtained through the extended oxidation of metallic potassium by nitrous oxide. Lupton[3] claimed to have obtained the oxide K_2O_2 by the direct oxidation of potassium but his work is uncertain. The compound K_2O_2 has not been definitely established as a result of the direct oxidation of potassium.

Harcourt obtained sodium peroxide, Na_2O_2 as a final direct oxidation product of sodium and this result has been confirmed by Holt and Sims as well as others. Rengade[4] obtained the suboxides Na_2O and K_2O as well as the corresponding oxides of cesium and rubidium by direct oxidation in the presence of excess metal and subsequent removal of this excess by distillation in a vacuum.

Joannis,[5] oxidizing the metals in liquid ammonia, obtained the oxide of sodium, Na_2O_2 and, as he believed, a trioxide Na_2O_3. He also obtained a product corresponding to the formula $Na_2O.NH_3$, which was doubtless a mixture of sodium hydroxide and sodium amide (Rengade[4]). He likewise recorded the oxides of potassium K_2O_2, K_2O_3 and K_2O_4.

Rengade made a careful study of the oxidation of cesium and rubidium

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[1] Harcourt, *J. Chem. Soc.*, **14**, 267 (1862).

[2] Holt and Sims, *ibid.*, **65**, 432 (1894).

[3] Lupton, *ibid.*, **30**, 565 (1870).

[4] Rengade, *Ann. chim. phys.*, [8] **11**, 348 (1907).

[5] Joannis, *Compt. rend.*, **110**, 1370 (1893).

in liquid ammonia and established the existence of the oxides corresponding to the formulas M_2O_4, M_2O_3 and M_2O_2. He states that with potassium similar results were obtained but gives no numerical data. Rengade showed that in the case of cesium and rubidium the product of oxidation in liquid ammonia depends upon the rate. With rapid oxidation the initial product corresponds to M_2O_2 and the final product to M_2O_4. On slow oxidation the initial product is a mixture of the hydroxide MOH and the amide MNH_2. The amide is further oxidized with the formation of nitrite and hydroxide.

According to deForcrand,[6] potassium tetroxide loses oxygen above its melting point with the formation of the trioxide, K_2O_3. Holt and Sims[2] found that the final product, on heating the tetroxide in glass, corresponds to the formula K_2O, reaction presumably taking place between the oxide and the glass.

The purpose of the present investigation was to determine the nature of the oxidation products obtained with sodium and potassium in liquid ammonia, to establish the reversibility of the dissociation of potassium tetroxide at higher temperatures and, if possible, to determine the equilibrium pressure of this process.

Oxidation of Potassium and Sodium in Liquid Ammonia

Apparatus and Procedure.—A detailed description of the apparatus employed in carrying out the oxidation of sodium and potassium in liquid ammonia may be omitted for the sake of brevity. The method consisted essentially in passing a controlled stream of oxygen through a solution of the metal in liquid ammonia contained in a weighed tube at liquid-ammonia temperatures. The volume of oxygen absorbed was measured and the weight of the products of reaction was determined by weighing the containing tube at the end of the reaction. The metal employed was melted in a vacuum and run into small sealed tubes of known weight. These tubes were broken just prior to introduction into liquid ammonia. The initial end-point of the reaction was indicated by the disappearance of the blue color characteristic of the free metal. The final end-point was obtained by passing oxygen through the solution until no further absorption occurred. In the rapid oxidation of the metal, a rapid stream of oxygen was passed through the solution under a considerable external pressure (20 cm.). In slow oxidation, a slow stream of oxygen was passed through the solution together with a stream of ammonia, the ammonia passing out under practically atmospheric pressure.

Mechanism of the Oxidation Process.—If the oxidation of potassium corresponds to that found by Rengade for rubidium and cesium we should expect the following reactions to occur.

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[6] deForcrand, *Compt. rend.*, 158, 991 (1914).

On initial rapid oxidation the dioxide is formed according to the equation,

$$K_2 + O_2 = K_2O_2 \qquad (I)$$

and, on further oxidation of this product, the tetroxide, according to the equation,

$$K_2O_2 + O_2 = K_2O_4 \qquad (II)$$

On slow oxidation, the dioxide is probably first formed and then reduced to the suboxide by excess metal present, the net result of these reactions being expressed by the equation,

$$K_2 + \tfrac{1}{2}O_2 = K_2O \qquad (III)$$

This oxide, being a salt of the very weak acid KOH, ammonolyzes according to the equation,

$$K_2O + HNH_2 = KOH + KNH_2 \qquad (IV)$$

On further introduction of oxygen, the amide is oxidized to nitrite according to the equation,

$$2KNH_2 + \tfrac{3}{2}O_2 = KOH + KNO_2 \qquad (V)$$

If K_2O_3 is formed it should appear as an intermediate product between Reactions I and II. In the case of sodium, Reaction II does not occur.

Slow Oxidation of Potassium.—Preliminary experiments with potassium, in which the volume of oxygen absorbed was measured, indicated the initial formation of K_2O_2 on rapid oxidation, and of a mixture of compounds on slow oxidation. The weight of the reaction product as determined in a series of experiments is given in Table I.

TABLE I

INITIAL PRODUCT OF SLOW OXIDATION OF POTASSIUM

Potassium, g.	0.1908	0.2757	0.1611
Product found, g.	.2795	.3961	.2296
Product calcd. for KOH + KNH_2, g.	.2713	.3921	.2291

As may be seen from the table, the weight of the product formed is in substantial agreement with that required for the formation of potassium hydroxide and potassium amide according to Equations III and IV. The products of initial oxidation were identified by separating the two materials. A weighed quantity of potassium was oxidized in one limb of a two-legged tube, the potassium amide formed, being soluble in liquid ammonia, was decanted into the second limb of the tube, the two limbs were separated and their contents weighed. Following are the results obtained: 0.3558 g. of potassium gave 0.2484 g. of KOH and 0.2625 g. of KNH_2, that required is, 0.2553 g. and 0.2507 g., respectively. The slight excess in the weight of potassium amide was doubtless due to the presence of a small quantity of hydroxide carried over in decanting the solution of the former. The liquid ammonia soluble product was identified as potassium amide by treating with water.

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Oxidation of Potassium Amide.—If, after disappearance of the blue color due to potassium, a stream of oxygen is passed through the solution further absorption of oxygen occurs. On completion of this oxidation process and evaporation of the solvent, the residue consists of a mixture of white and slightly yellow materials. A number of reactions were carried out in which the volume of oxygen absorbed and the weight of the final products of oxidation were determined. The results are given in Table II.

TABLE II

FINAL PRODUCTS OF SLOW OXIDATION OF POTASSIUM

K, g.	O_2 calcd., cc.	O_2 used, cc.	$KOH + KNO_2$, g Calcd.	 Found
0.1890	81.2	75.6	0.3413	0.3326
.2621	..	..	.4733	.4645
.2457	105.6	101.0	.4438	.4395
.2003	86.0	85.8	.3618	.3606

As may be seen, the volumes of the oxygen absorbed and the weights of the final products of oxidation are in substantial agreement with those required for the formation of potassium hydroxide and potassium nitrite according to Equations III, IV and V. The weights found as well as the volumes of oxygen used are a trifle lower than those required. This is probably due to incomplete oxidation. The final product was readily soluble in water and answered to tests for nitrite and hydroxide.

A weighed quantity of potassium amide was oxidized in one limb of a two-legged tube and, on completion of the oxidation process, the products were separated by decanting the solution of potassium nitrite from the hydroxide; 0.3401 g. of potassium converted to amide yielded, after oxidation and separation, 0.2526 g. of KOH, while that required is 0.2440 g. A portion of the potassium nitrite that separated in this reaction was lost on evaporating the solution. Titration with potassium permanganate showed that this product consisted primarily of potassium nitrite.

An attempt was made to oxidize potassium amide in the absence of ammonia. On slowly admitting oxygen absorption occurred, the color of the material changing to bright yellow and then to orange. After the initial reaction, the rate of absorption was slow and the weight of the materials indicated that the reaction was incomplete, at the end of 12 hours. The contents of the tube answered to the tests for potassium nitrite, and a measurable quantity of ammonia was recovered with the excess oxygen. These facts indicate that the oxidation of potassium amide in the dry state is similar to that in liquid ammonia. The color changes are rather puzzling.

Rapid Oxidation of Potassium.—The dioxide K_2O_2 is formed when potassium is rapidly oxidized in liquid ammonia and the process of oxidation is interrupted as soon as the free metal has disappeared. The dioxide is white, but at times is tinted faintly yellow, probably owing to the presence of a trace of the tetroxide. The dioxide does not react with liquid ammonia even on long standing. It is readily oxidized to the tetroxide on passing oxygen through its liquid ammonia suspension.

The results of a series of experiments are given in Table III.

TABLE III

PRODUCTS OF RAPID OXIDATION OF POTASSIUM

K, g.	O_2 for K_2O_2, cc		O_2 for K_2O_4, cc.,		K_2O_2, g		K_2O_4, g	
	Calcd	Obs.	Calcd.	Obs.	Calcd.	Obs	Calcd	Obs.
0.1840	...	...	..	...	...	...	0 3346	0.3274
.1946	55.7	55.0	111.4	112.0	...	...	.3539	3540
.1979	...	...	113.4	114.0	...	...	.3599	3547
.3362	96.3	95.0	...	...	...	...	.6115	.6056
.2520	72.2	74 3	144.4	145 0	...	...	.4583	4564
.2411	69.1	68.7	...	...	...	...	4385	.4340
.2762	79.1	77.5	...	...	0.3993	0.3951	...	...
.4123[a]	118.1	106 0	...	...	.5811	.5683	...	...
.5147[a]	147.5	138 0	...	...	.7253	.7094	..	...
.4336[a]	124.2	113.0	...	...	.6162	.6037	...	...

[a] *Weighed in air.*

The volumes of oxygen absorbed and the weights of the resulting products correspond with those required for the oxides K_2O_2 and K_2O_4. No evidence was found indicating the existence of the intermediate oxide K_2O_3. At times, the precipitate had a slightly reddish tint but the volume of oxygen absorbed and the weights indicated a mixture of two or more oxides. Under the conditions of the present experiments, no product could be separated corresponding to the formula K_2O_3.

The tetroxide K_2O_4 is comparatively stable; it is not affected by dry air but it reacts slowly with moisture. On treating it with water, one molecule of oxygen is evolved according to the equation

$$K_2O_4 = K_2O_2 + O_2 \tag{VI}$$

This confirms the observations of the earlier investigators.

The dioxide is extremely reactive. In one case, on admitting air into a tube containing about 0.5 g. of this oxide, the product turned orange-red with evolution of considerable heat. On admitting water an explosion occurred. In another case the product turned reddish-brown on admission of air, after which explosion occurred. After explosion the products in various parts of the tube were colored red, yellow and purple. Holt and Sims prepared a product corresponding to the formula K_2O_3 by treating metallic potassium with nitrous oxide. This product they found to be extremely reactive with respect to oxygen.

An attempt was made to oxidize finely divided potassium in pure oxygen. The metal was obtained in a finely divided state by dissolving it in liquid ammonia and then evaporating the solution rapidly. On admitting oxygen, rapid absorption took place, at first, but the rate slowed with time. At the end of six weeks 0.2239 g. had absorbed only 0.0792 g. of oxygen. On initial admission of oxygen (at low pressure) the surface of the metal turned blue and after standing some time a red color developed at certain points. At the end of a week a cream-colored product made its appearance. On longer standing it was observed that the initial product gradually turned red and that this in turn passed over into the cream-colored material.

Oxidation of Sodium in Liquid Ammonia.—On rapid oxidation of sodium the peroxide Na_2O_2 is formed. This oxide is stable in liquid ammonia. No evidence was found of the formation of an oxide of oxygen content higher than Na_2O_2. This is contrary to the observations of Joannis who claimed to have obtained an oxide Na_2O_3. The results of several experiments, in which the volume of absorbed oxygen was measured, follows: sodium, 0.1370 and 0.2080 g.; O_2 absorbed, 69.8 and 104.2 cc.; O_2 required, 66.7 and 101.3 cc.

On slow oxidation, sodium hydroxide and sodium amide are initially formed according to Equations III and IV. On further treatment with oxygen, the amide is converted to a mixture of sodium hydroxide and sodium nitrite according to Equation V. The results of several experiments follow: 0.1482 g. of sodium slowly oxidized absorbed 38.5 cc. of oxygen at the end of the first stage and 91.0 cc. at the end of the final stage of oxidation. The final product weighed 0.3028 g. Corresponding to Equations III, IV and V, the volumes required are 36.1 and 90.2 cc., respectively, and the final weight, 0.3044 g.

0.1429 G. of sodium was converted to the amide and oxidized. There was absorbed 105.0 cc. of oxygen, and the final weight was 0.3243 g. According to Equation V, there are required 104.4 cc. and 0.3387 g., respectively. The solution of the final product answered to tests for nitrite.

The highest oxide of sodium in liquid ammonia is Na_2O_2. On slow oxidation, sodium, like potassium, is oxidized to hydroxide and nitrite.

Dissociation of Potassium Tetroxide at Higher Temperatures

Final Products of Dissociation.—Known weights of potassium tetroxide, usually in the form of pellets, were introduced into weighed Pyrex or soda-glass tubes and heated to the melting point of the oxide. Before being heated, the tubes were evacuated. The oxygen evolved on heating was removed by means of a Toepler pump and its volume determined. At the end of the reaction the tubes containing the material were detached and weighed.

When the tetroxide is heated for some time in contact with glass, reaction takes place, oxygen is evolved, and the weight of the final product corresponds to the formula K_2O. The results of several experiments follow: K_2O_4, 0.3205, 0.1914 g.; final product, 0.2276 and 0.1193 g.; required for K_2O, 0.2344 and 0.1269 g. These results are in agreement with earlier observations of Holt and Sims.

In several cases, particularly when the surface of contact between the oxide and the glass container was small, the weight of the final product was found to correspond to K_2O_2 and this product when dissolved in water answered to tests for hydrogen peroxide. The results of one of these experiments follow: K_2O_4, 0.2098 g.; final weight, 0.1694 g.; required for K_2O_2, 0.1626 g.

The evolution of oxygen at higher temperatures is greatly influenced by moisture. Potassium tetroxide which has been carefully guarded against the action of moisture shows practically no evolution of oxygen in a vacuum until the temperature is raised to 300° or higher. When the oxide has been exposed to the action of moisture, evolution of oxygen begins at about 100° and continues until approximately 200° is reached, when it ceases. The amount of oxygen evolved at these temperatures is dependent upon the extent to which the material was originally exposed to the action of moisture. Once this initial evolution of oxygen has taken place, further evolution of oxygen does not occur until a temperature of 300° is reached, after which the behavior of the material corresponds closely with that of dry potassium tetroxide. For example, in one case, 0.2601 g. of material when exposed to the action of water vapor at room temperature yielded 7.66 cc. of oxygen and, on heating to 270°, evolved 29.8 cc. of oxygen, while after heating to temperatures above 300°, yielded only an additional 8.4 cc. of oxygen. The weight of the residue on completion of the dissociation process was found to be 0.1959 g. as compared with 0.2100 g. required for K_2O_2. The total volume of gas evolved was 38.2 cc. as compared with 35.1 cc. required for K_2O_2 as final product. Just what part water plays in the dissociation of potassium tetroxide between 100° and 200° could not be determined from the present experiments.

In order to avoid the action between the oxide and the glass containing tube, pellets of dry tetroxide were placed in a gold or an aluminum cup in a weighed Pyrex tube. Gold was found to be much less resistant to the action of the oxide than is aluminum. A gold cup weighing 1.6503 g. lost 24.2 mg. after having been heated to the melting point of the tetroxide for about an hour. On the other hand, an aluminum cup exposed to the action of the tetroxide at 500° for more than an hour showed no appreciable loss in weight. However, on extended heating of the tetroxide in an aluminum cup (30 hours) the surface of the aluminum appeared to have suffered attack. Using an aluminum cup, the weight of the residual oxide was found to correspond approximately to that required for K_2O_3. It was noticeable that the color of the final product was markedly darker than that of the original tetroxide. At ordinary temperatures the tetroxide is distinctly yellow while the final product was of an orange color.

A pellet weighing 0.1173 g. lost 0.0175 g. on extended heating above the melting point and the residue weighed 0.0998 g.; the weight required for K_2O_3 is 0.1041 g. In another experiment, 0.1102 g. of K_2O_4 lost 0.0123 g., and the residue weighed 0.0950 g.; the weight calculated for K_2O_3 is 0.0977 g.

The weight of the final product is 7% below that required for K_2O_3. This may in part be due to a slight action of the oxide on the aluminum cup. Our observations with respect to K_2O_3 in general confirm the earlier work of deForcrand.

Reversibility of Dissociation Process.—A sample of the tetroxide in an aluminum cup was heated to 370°, 400° and 460°, first in a vacuum and then in the presence of oxygen at a pressure of one atmosphere. The loss and gain in weight of the oxide are given in Table IV. The total weight of tetroxide was 0.1102 g.

TABLE IV

LOSS AND GAIN IN WEIGHT OF K_2O_4 AT DIFFERENT TEMPERATURES

Temp., °C.	370	400	460
Loss, g.	0.0057	0.0099	0.0123
Gain, g.	0.0021	0.0099	0 0123

The loss corresponding to one atom of oxygen per molecule of K_2O_4 is 0.0125 g. At 370° the loss of 0.0057 g. was much below this value. On treating with oxygen, the original weight was not reëstablished. At 400° the loss was markedly higher although still below the amount required for K_2O_3 as final product. On treating with oxygen at 400° the initial weight, prior to heating in a vacuum, was reëstablished. At 460° the loss of 0.0123 g. corresponds closely to that required for K_2O_3 as final product. On heating the material in oxygen the additional weight was reëstablished. The weight of the final product, after evacuating at 470°, was 0.0950 g. as compared with 0.0977 g. for K_2O_3. This difference may have been due to the presence of a trace of moisture which would lead to the formation of K_2O_2 at temperatures between 100 and 200°. The final material exhibited a marked orange color. It is clear from these results that the process of dissociation of K_2O_4 at higher temperatures is a reversible one.

The Dissociation Pressure of K_2O_4.—Since the dissociation process is reversible, it might be expected that the equilibrium pressure could be determined. According to observations of deForcrand at 480°, the dissociation pressure is not fixed owing to the fact that the system contains only a liquid and a vapor phase and is therefore divariant. An attempt was made to determine the equilibrium pressure at temperatures below 400°, where apparently no liquid phase is present. It was found, however, that even at these temperatures, the pressure is dependent upon the volume of oxygen evolved.

A pellet of potassium tetroxide weighing 0.1271 g. was placed in a large aluminum cup within a Pyrex tube which was attached to a high-vacuum pump and to a calibrated McLeod gage. The tube containing the pellet was raised to 180° and thoroughly evacuated. It was then allowed to cool to room temperatures, after which the temperature was again raised and a series of pressure observations made. The results of the first series of observations are given in Table V.

TABLE V

DISSOCIATION PRESSURE OF POTASSIUM TETROXIDE AS INITIALLY MEASURED

t, °C.	100	120	155	195	237	247	300	305
p, mm. of Hg	0.035	0.055	0.095	0.295	0.465	0.532	1.47	1.61

At 200° the color of the oxide was orange while at 300° it was practically black. When the tube was pumped for a short time at 305°, the pressure returned to 0.170 mm. after standing for about an hour. The tube was allowed to cool without evacuating and left for 24 hours. At the end of that time the following series of pressure readings was made.

TABLE VI

PRESSURE OF K_2O_4 AT DIFFERENT TEMPERATURES AFTER PUMPING

t, °C.	24	60	100	160	205	263	280	300
p, mm. of Hg	0.010	0.011	0.012	0.015	0.018	0.071	0.114	0.206

After removing the evolved gas at 300°, the pressure returned practically to its original value but on continued pumping it returned to a lower value. After pumping had been continued for 16 hours at 300°, the pressure returned to 0.170 mm. The weight of the oxide at this time was found to be 0.1198 g. On further pumping for 17 hours at 300° the pressure returned to 0.128 mm. at the end of one hour. The weight was found to be 0.1073 g.

Corresponding to the equation

$$K_2O_4 = K_2O_3 + \tfrac{1}{2}O_2 \qquad \text{(VII)}$$

0.1271 g. of K_2O_4 should lose 0.0146 g. At the end of the first 16 hours' pumping at 200°, the loss was 0.0073 g. and at the end of another 17 hours the total loss was 0.0098 g. The total weight of oxygen removed was well below that required according to Equation VII. On the first pumping at 300° for a short time the pressure fell from 1.61 mm. to 0.170 mm. The loss in weight was not determined but on pumping for 16 hours at 300°, the pressure again returned to 0.170 mm., 0.0073 g. of oxygen having been lost. On pumping for another 17 hours at 300° with an additional loss of 0.0025 g. the pressure returned to 0.13 mm. in one hour. It appears that at 300° the equilibrium pressure of reaction (VII) may lie in the neighborhood of 0.17 mm. The observations recorded in Tables V and VI are not true equilibrium pressures.

Summary

1. On slow oxidation of potassium in liquid ammonia, potassium hydroxide and potassium amide result as initial products. On further oxidation, potassium amide yields potassium hydroxide and potassium nitrite.

2. The dioxide, K_2O_2, is formed as initial product of rapid oxidation of potassium in liquid ammonia. On further oxidation this yields the tetroxide, K_2O_4. No evidence was found indicating the formation of the trioxide, K_2O_3, in liquid ammonia.

3. The products of slow oxidation of sodium in liquid ammonia correspond to those of potassium. On rapid oxidation, the dioxide, Na_2O_2, is formed. No evidence was found indicating the formation of the trioxide, Na_2O_3.

4. Potassium tetroxide, K_2O_4, dissociates at temperatures above 300°. This process is reversible but the pressures appear to depend on the oxygen content of the solid phase. The final product of dissociation has a composition corresponding to the formula, K_2O_3.

5. Potassium tetroxide exposed to the action of moisture loses oxygen irreversibly between 100° and 200°.

PROVIDENCE, RHODE ISLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF IOWA STATE COLLEGE]

THE DECOMPOSITION OF POTASSIUM CHLORATE. II. THE SPONTANEOUS DECOMPOSITION TEMPERATURES USING VARIOUS PROPORTIONS OF MANGANESE DIOXIDE, AND OF FERRIC OXIDE, AND OF A MIXTURE OF MANGANESE DIOXIDE AND FERRIC OXIDE AS CATALYSTS[1]

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Spontaneous decomposition temperatures for potassium chlorate-manganese dioxide mixtures,[2] and for iron oxide-manganese dioxide mixtures[3] have been reported. Spontaneous decomposition temperature was defined as the temperature at which the mixture began to evolve oxygen violently with a rapid rise of temperature due to the heat of reaction. The catalysts used for the determinations previously reported were not especially purified. The manganese dioxide may have contained some ferric oxide which Neville[4] has shown acts as a promoter for manganese dioxide in catalyzing the decomposition of potassium chlorate. The ferric oxide either had been heated to high temperatures, which destroys much of its catalytic activity, or contained ammonium chloride which according to Hodgkinson and Lowndes[5] lowers the decomposition point of potassium chlorate.

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[1] This paper is an abstract of a thesis presented by J. Austin Burrows in partial fulfilment of the requirements for the degree of Doctor of Philosophy at Iowa State College.

[2] Brown, Burrows and McLaughlin, THIS JOURNAL, **45**, 1343 (1923).

[3] Brown and White, *Proc. Iowa Acad. Sci.*, **31**, 291 (1924).

[4] Neville, THIS JOURNAL, **45**, 2330 (1923).

[5] Hodgkinson and Lowndes, *Chem. News*, **58**, 309 (1888); **59**, 63 (1889).

The object of the present work is to determine the spontaneous decomposition temperatures of potassium chlorate with the individual catalysts, using carefully purified oxides, and to find the correlation between the promoter action of ferric oxide reported by Neville and the effect of ferric oxide-manganese dioxide mixtures in causing spontaneous decomposition of potassium chlorate.

Materials

The potassium chlorate used was the c. p. grade of the Baker and Adamson Chemical Company which had been analyzed by Dr. H. M. McLaughlin in this Laboratory and found free from chlorides, heavy metals, calcium bromates, nitrates and sulfates, and except for a small amount of adsorbed moisture was pure potassium chlorate.

The manganese dioxide was prepared from Merck's highest purity c. p. carbonate by heating it in air to 255–260° during frequent stirring, until free from carbonate. After it had been washed thoroughly with dil. hydrochloric acid and water, it was found to be free from iron, nickel, silver and ammonium compounds. The oxidizing power was determined by dissolving it in sulfuric acid, adding an excess of oxalic acid, and titrating back with potassium permanganate; 0.4 g. required 72.82 cc. of 0.0981 *N* oxalic acid as compared with 91.5 cc. required for pure manganese dioxide. The total manganese content was determined by the bismuthate method; 0.01 g. of the manganese dioxide oxidized 11.76 cc. of 0.0496 *N* ferrous sulfate solution, as compared with 11.59 cc. required for pure ferrous sulfate. This discrepancy is probably due to the presence of moisture and lower oxides of manganese. A lower oxide of manganese would not be an impurity for our purpose as alternate oxidation and reduction of the catalysts is believed to occur,[5] and we find manganese carbonate almost as effective a catalyst as manganese dioxide.

The ferric oxide was prepared from Merck's reagent ferric chloride by precipitation with sodium hydroxide in an iron container, washing by decantation, and drying for two weeks at 110°. The sodium hydroxide had been freed from carbonates by filtering through iron filings in a paraffined Gooch crucible. The iron content of the oxide indicated 98.5% ferric oxide. It was free from manganese, silica, nickel and chlorides.

Apparatus

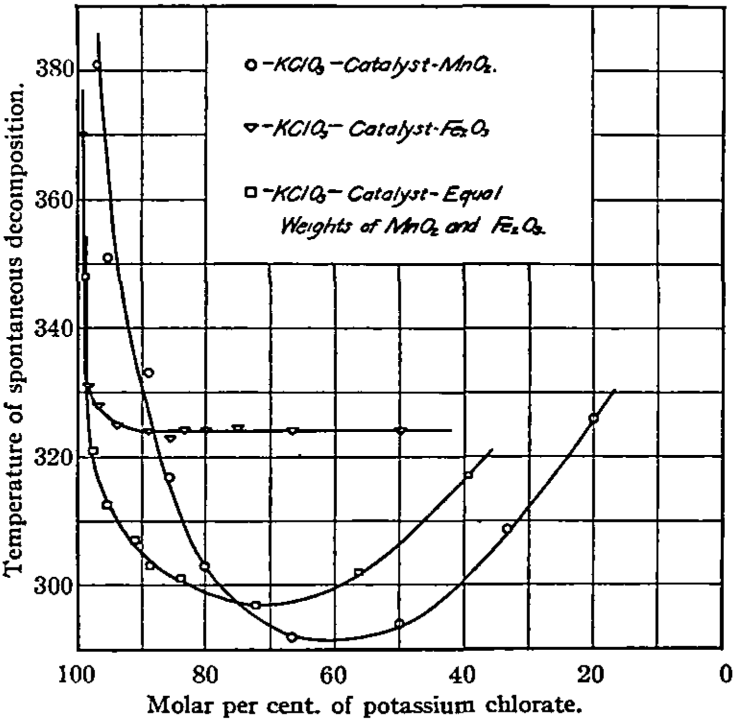
The apparatus was essentially the same as that used by Brown, Burrows and McLaughlin.[2] The furnace was electrically heated and regulated. In the bottom of the furnace was placed a vessel containing a low-melting alloy which reduced the fluctuations of temperature. The temperatures were taken by mercury thermometers, one imbedded in the reacting mixture and another suspended in the furnace near the tube containing the reacting mixture.

Experimental

Each ingredient was dried at 110°, pulverized, and sifted through a 200-mesh sieve. The mixtures were made by sifting proper proportions of the ingredients together once through a 200-mesh sieve and twice through a 150-mesh sieve. The resulting mixtures appeared uniform.

Manganese Dioxide as Catalyst

Mixtures were prepared in which the number of moles of manganese dioxide per hundred moles of mixture were 3.0, 5.9, 11.1, 14.3, 20.0, 33.3, 50.0, 66.7 and 80.0. Portions of each of the mixtures containing 2 g. of potassium chlorate were placed in a hard glass, side-arm test-tube 2.5 cm. in diameter. The tube was lowered into the furnace which had been heated to a temperature such that the insertion of the tube would lower it to approximately the spontaneous decomposition temperature. The spontaneous decomposition temperature is marked by a sudden acceleration of temperature rise in the reaction tube and a spurting of water from the collecting bottle due to rapid evolution of oxygen. Three or more portions of each mixture were heated and the spontaneous decomposition temperature reported is the average of the temperatures observed for that mixture. These temperatures are plotted against molal composition in Fig. 1, each point being indicated by a circle.



Ferric Oxide as Catalyst

Mixtures were prepared in which the moles of ferric oxide per 100 moles of mixture were 0.8, 1.6, 3.0, 5.9, 11.1, 14.3, 16.7, 20.0, 25.0, 33.3, 50.0, 66.7, 80.0, 83.3, 85.6 and 88 8. When 100 moles of mixture included as much as 66.7 moles of ferric oxide no sudden rise in temperature or spurting of water occurred. In Fig. 1 is a graph of the spontaneous decomposition temperatures of the other mixtures plotted against molar composition, each point being indicated by a triangle.

Mixtures of Manganese Dioxide and Ferric Oxide as Catalyst

Equal weights of manganese dioxide and ferric oxide[6] were intimately mixed. Portions of this mixture were then mixed with potassium chlorate in such proportions that the moles of combined catalysts in 100 moles of the final mixtures were 1.2, 2.4, 4.6, 8 8, 11.4, 16.2, 27.9, 43.6 and 60.6. The spontaneous decomposition temperatures with the mixed catalyst are plotted against the molar concentrations in Fig. 1, the points being indicated by squares.

Discussion of Results

The data given strengthen the conclusions which the authors established in their previous paper, namely, that the spontaneous decomposition tem-

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[6] Neville, Ref. 4, found this to be the most effective proportions.

perature of mixtures of potassium chlorate and manganese dioxide depends upon the percentage composition of the mixture and that those containing too much manganese dioxide as well as those containing too little manganese dioxide suffer no spontaneous decomposition. This is believed to be due in the former case to the fact that the heat given off by the potassium chlorate which would otherwise be utilized in increasing the rate of its decomposition is not sufficient to do this as well as to increase the temperature of the large amount of inert material which is present. In the latter case no spontaneous decomposition is produced due to the fact that much of the potassium chlorate is not in contact with the catalyst since too little catalyst is present.

In general it is noted that ferric oxide is not as efficient as a producer of spontaneous decomposition as manganese dioxide although at some of the concentrations in which very little catalyst was present, the ferric oxide gave a spontaneous decomposition temperature lower than manganese dioxide. This is very probably due to the fact that the ferric oxide was in a very much finer state of division than the manganese dioxide since much of it was practically colloidal. This gave an enormous surface and, therefore, the small amount of the ferric oxide could be in contact with a large amount of potassium chlorate and thus catalyze its decomposition. This work, as well as that of Brown and White, establishes the fact that for a wide variety of mixtures of potassium chlorate and ferric oxide there is a constant spontaneous decomposition temperature. The reason for this has not been determined.

Neville has shown[4] that at constant temperatures ferric oxide added to mixtures of potassium chlorate and manganese dioxide acts as a promoter of the catalysis. The most efficient proportion is ferric oxide and manganese dioxide in equal weights. Our data show that such a mixture is a more efficient producer of spontaneous decomposition of potassium chlorate than manganese dioxide alone or ferric oxide alone when the proportion of catalyst is less than 25%. But a potassium chlorate–manganese dioxide mixture containing between 25 and 55% of manganese dioxide has a lower spontaneous decomposition point than any mixture containing potassium chlorate and equal weights of ferric oxide and manganese dioxide. It is difficult to think of ferric oxide as a promoter of this particular phenomenon, spontaneous decomposition of potassium chlorate in the presence of manganese dioxide at all concentrations. If a mixture of 20 moles (1738.6 g.) of manganese dioxide with 80 moles of potassium chlorate is chosen, the spontaneous decomposition temperature is about 303°. If 1738.6 g. (10.9 moles) of ferric oxide is added there will be $(30.9/110.9) \times 100 = 27.9$ moles of catalyst per hundred moles of mixture and the spontaneous decomposition temperature is 297°. If 1738.6 g. (20 moles) of manganese dioxide is added to a similar mixture there will be (40/120) × 100 = 33.3 moles of catalyst per hundred moles of mixture and the spontaneous decomposition temperature is 292°. That is, the addition of manganese dioxide to manganese dioxide produces almost twice as great a lowering of the spontaneous decomposition point as is produced by the addition of an equal weight of ferric oxide, a supposed promoter. It is just as evident from an inspection of Fig. 1, that doubling the manganese dioxide content in manganese dioxide–potassium chlorate mixtures containing less than 10 moles of manganese dioxide per 100 moles lowers the spontaneous decomposition point less than it would be lowered by doubling the weight of catalyst by adding ferric oxide.

The authors wish to express their appreciation to Dr. H. M. McLaughlin for helpful suggestions during the progress of the work.

Summary

1. For a wide range of mixtures manganese dioxide produces a lowering of the decomposition temperature of potassium chlorate and the amount of heat produced by the decomposition of part of it is sufficient to cause spontaneous decomposition of the remainder. This spontaneous decomposition takes place at very definite temperatures for each mixture under defined conditions.

2. Ferric oxide also causes spontaneous decomposition of potassium chlorate over a wide range of mixtures.

3. The spontaneous decomposition temperature for ferric oxide mixtures is quite constant for a wide variety of mixtures.

4. When manganese dioxide is present in mixtures of that substance with potassium chlorate in proportions less than 25% of the total number of molecules, the substitution of ferric oxide for one-half of the weight of manganese dioxide present produces a lowering of the spontaneous decomposition temperature; when more than 25% of the molecules in the mixture are manganese dioxide, the substitution of ferric oxide for one-half of the weight of manganese dioxide produces a rise in spontaneous decomposition temperature.

5. The substitution of manganese dioxide for one-half of the ferric oxide in mixtures of that substance with potassium chlorate lowers the spontaneous decomposition point for all proportions of catalyst except those containing very little catalyst.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE]

THE INTERPRETATION OF ADSORPTION ISOTHERMS AND ISOSTERES

BY ALBERT SPRAGUE COOLIDGE

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When experiments are made upon the adsorption of vapors by a porous adsorbent, and the quantities found to be adsorbed at a particular temperature are plotted against the logarithms of the relative pressures (observed pressures divided by the vapor pressure of the free liquid at the same temperature), curves of the general scope of Curve 1, Fig. 1, are obtained. Let P be the relative pressure, Q the quantity adsorbed (in any convenient unit of measurement); then the lower portion of the curve will be in approximate agreement with the familiar Freundlich equation, $\log P = a \log Q + b$. At higher values of Q, this relation ceases to hold; the curve becomes nearly straight, shows a rather sudden bend at the point marked "A," and appears to terminate suddenly, having a finite slope, at "B," where $P = 1$, and the system is therefore saturated. However, as I have shown in a previous paper,[1] this sudden termination actually occurs only at temperatures below the freezing point of the liquid. Above this temperature, the isotherms bend upward when the relative pressure is just less than unity, and approach as asymptote the line $\log P = 0$, so that no definite quantity can be said to be adsorbed at saturation. The dashed line near "B," Fig. 1, represents this behavior on an exaggerated scale. This portion of the isotherm is generally ignored. We shall assume that it is due to some secondary effect, and that the isotherm of true adsorption runs as drawn right up to the point of saturation, "B." This assumption is justified partly because no progress can be made without it in studying the phenomena of saturation, and partly because the ultimate capacities of the system, as thus determined for various substances and at different temperatures, show many regularities, and evidently correspond to something real.

There appears to have been put forward no satisfactory interpretation of the characteristic form of the adsorption isotherm, especially of the manner in which it approaches saturation. Most theories start by assuming a particular isotherm as experimentally given, and attempt to derive therefrom all other isotherms. Langmuir's[2] simplest equation gives isotherms showing points of inflection and definite ultimate capacities, but the latter are reached only at infinite pressures. Williams[3] has derived the equation $\log a/c = A_0 - A_1 a$, where a is the amount adsorbed, c the concentration in the gas phase, A_0 and A_1 are constants. For moderate values of a,

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[1] Coolidge, THIS JOURNAL, 46, 609 (1924).

[2] Langmuir, *ibid.*, 40, 1361 (1918).

[3] Williams, *Proc. Roy. Soc.* (London), 96A, 287 (1919).

such that A_1a greatly exceeds log a, this is in agreement with the straight portion already noted, just to the left of "A," Fig. 1. The equation does not claim to hold up to saturation.

It strikes me that the suddenness with which saturation is reached is very surprising. When the vapor-pressure curve of a solid or liquid, plotted against temperature, or that of a solution plotted against concentration, shows a sudden change in slope, the physical chemist looks for the appearance of a new phase. In the case of an adsorption pushed beyond saturation, no one doubts that the excess of vapor introduced condenses to ordinary liquid (except below the freezing point). But it is hard to see how this can be considered a new phase, since it is generally believed that the adsorbed vapor itself, or at least its superficial layers, are already in the form of the liquid, evaporation being hindered by the operation of some force caused by the proximity of the adsorbent. It is not easy to understand why this force should suddenly cease to act. Furthermore, if saturation means the formation of a new phase, it should be possible by careful work to delay its appearance and to produce a supersaturated adsorption (analogous to a supersaturated solution). This I have been able to do[1] below, but not above, the freezing point, which apparently proves that while the solid appears as a new phase, the liquid does not. A possible explanation of the suddenness of saturation, which involves neither of these difficulties, will be suggested in this paper.

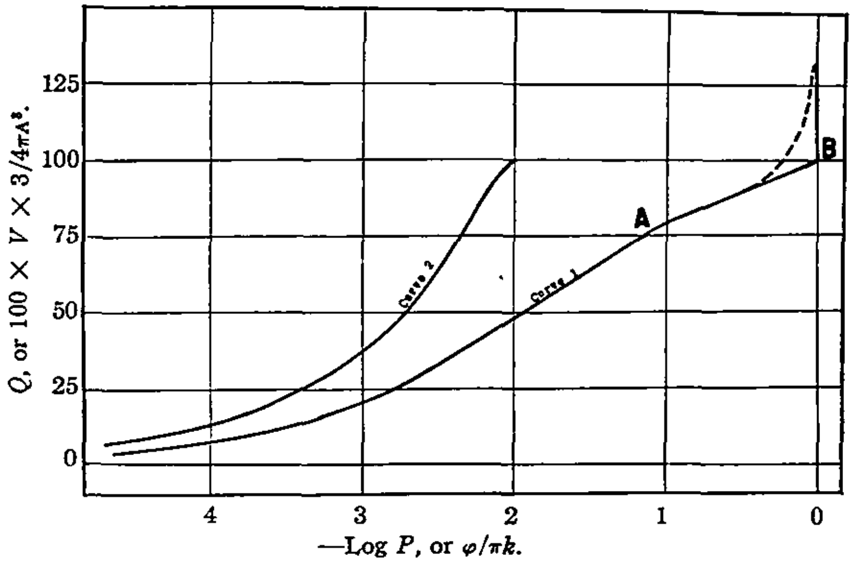

Fig. 1.

The idea that adsorbed vapors condense to something resembling the normal liquid state is based primarily on the experimental fact that the quantities of different vapors necessary to saturate a given adsorbent are nearly the same as those required to produce, when condensed, a fixed volume of normal liquids. This will appear from Table I, taken from my data[1] for activated coconut charcoal. In this table, the second column gives the volume of normal liquid, in cubic centimeters, which would be produced at 0° by the quantity of the indicated vapors which suffices to saturate 1 g. of charcoal at 0°. The third column, which will be needed later, gives the apparent specific volume of a similar charcoal, as measured by Harkins and Ewing with the corresponding liquids; the fourth is the sum of the second and third, and the fifth is the compressibility of the liquid. (This has been taken where possible from 0 to 500 atmospheres at 0°; but in some cases where data were lacking, the value at 20° from 300 to 500 atmospheres has been substituted as being roughly comparable.)

TABLE I

VOLUME AND COMPRESSIBILITY RELATIONS

1	2	3	4	5
Hg	(0.000)	1.156	(1 156)	4
H_2O	.424	0.543	0.967	41
CCl_4	.435	..	..	73
$CHCl_3$	.442	.502	.944	70
CS_2	.450	.486	.936	66
CH_3OH	.450	..	..	80
$HCOOC_2H_5$	.454	..	..	..
C_6H_6	.467	.498	.965	67
CH_3COOCH_3	.490	..	..	73
$(C_2H_5)_2O$	.494	.472	.962	107

It is strongly suggested that the adsorbent presents a fixed volume, rather than a fixed surface, where adsorption can occur, and that when this volume is exactly filled the system is saturated, showing the same vapor pressure as the free liquid. The surface layer is to be considered as identical in state with that of the free liquid, and to be under no additional forces. Such forces appear as soon as the amount of liquid present is insufficient to fill the adsorption space. If, in spite of being under these forces, the superficial liquid layer may be assumed to preserve its identity of state with that of the free liquid, then the work which an evaporating molecule has to do against the additional forces producing adsorption may be calculated, according to kinetic theory, by the equation $\varphi = -kT \ln P$, in which φ is the work desired, k the Boltzmann constant, T the absolute temperature, and P, as before, the relative pressure. The assumption seems to me a precarious one, but as it is generally made or implied in the development of theories of this class, we shall retain it unless it proves untenable.

Concerning the nature of the forces against which this work is done, two hypotheses are current. According to one, they are simply the cohesional attraction of neighboring adsorbed molecules, supposed to act with more than normal vigor because of the concavity of the liquid surface. It is well known that the relative pressure over such a surface should be given by the equation $\ln P = -2\sigma v/rRT$, in which σ is the surface tension, v the molecular volume, and r the mean radius of concavity. If we agree to assume that this effect is the sole cause of adsorption (that is, that none of the superficial molecules experience any direct attraction by the adsorbent), then it is still not possible to predict the form of any isotherm, since we do not know how the radius of concavity should vary with the degree of saturation. But if we make the additional assumption that the angle of contact between liquid and adsorbent is always zero, then we can use a single experimental isotherm as a basis for predicting others. For the radius r should be a function solely of the volume actually occupied by liquid (for a given specimen of adsorbent). The contour of the liquid surface is determined by the condition that its area, plus that of the film covering projecting portions of the adsorbent, must be a minimum consistent with the enclosure of a specified volume; these conditions contain no reference to specific properties of the liquid, or to temperature (except in so far as the adsorbent itself expands, which must be very little). Assuming the liquid to have its normal density, the relationship between radius and volume can be found empirically from a single isotherm, and the theory tested by seeing to what extent points on other isotherms can be predicted. A few examples will show how far from successful it proves.

Consider first my data[4] for activated coconut charcoal, taking benzene, the most carefully studied vapor, as standard. When, at 0°, enough benzene has been adsorbed to fill a space of 0.2 cc. with subcooled liquid at normal density (about half the ultimate capacity), the pressure of the system is 0.0055 mm., so that $-\log P = 3.68$. Taking $\sigma = 32$ and $v = 86.9$, we get $r = 2.89 \times 10^{-8}$ cm. Overlooking the fact that this radius is already of molecular magnitude, let us use it to predict the relative pressure under different conditions, but always with enough vapor adsorbed to fill 0.2 cc. with normal liquid at the temperature in question.

Substance	Benzene	Benzene	Carbon disulfide	Ether	Water
Temperature, °C.	99	150	0	0	0
—log *P*, calculated	1.82	1.19	2.65	2.51	1.80
—log *P*, observed	2.74	2.44	2.60	4.0	0.26

It has been supposed that the capillary condensation theory under discussion may hold better in the case of inert adsorbents like silica gel. Suitable data for a test are given by McGavack and Patrick.[5] Interpolating from their Fig. 8, we find for a volume of 0.1 cc. of sulfur dioxide at 0°, that $-\log P = 1.54$, whence, using their data for σ and v, r is found to be 3.16×10^{-8}. On this basis, the calculated relative pressures should, at —80° and at 100°, have the negative logarithms 2.99 and 0.47, instead

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[4] Ref. 1, p. 611.

[5] McGavack and Patrick, This Journal, **42**, 946 (1920).

of the observed 1.71 and 1.16, always for 0.1 cc. of liquid sulfur dioxide. As in the system benzene-charcoal, it is evident that the actual temperature coefficient is much less than that demanded by the theory.

Since the relative pressure for equal volumes increase with the temperature, the volumes for equal relative pressures must decrease with rising temperature. In this fact, McGavack and Patrick see confirmation of the capillary condensation theory. Owing to the pull of the concave meniscus, they reason that the liquid must be in a state of negative pressure, under which it will be distended the more, the higher is the temperature and in consequence the compressibility. The volume as calculated from the normal liquid density will, therefore, be smaller than that actually occupied, by an amount increasing with the temperature. The actual volume occupied they believe to be the same at all temperatures, for a given relative pressure. However, this last idea is untenable; the relative pressure for a given volume must have, in general, a temperature coefficient, since it is given by an equation which contains not only r, which is independent of temperature, but also σ, v and T, which vary with the temperature. As we have noticed, the effect of these variations alone, neglecting any changes in compressibility, gives a theoretical change of P with T for constant volume, and therefore of volume for constant P, which greatly exceeds observed values. The correction advocated by McGavack and Patrick would only increase the discrepancy. These authors believe that the ordinary relation between P and r, as given, is not valid for very small values of r. This seems probable, but there is no reason to suppose that the quantities σ v, and T cease to be involved, and therefore to confer a temperature coefficient upon P.

Further objections to the ideas of McGavack and Patrick suggest themselves. The negative pressure ought not to increase with temperature, as they believe, but to decrease, in proportion to σ, since σ measures the direct cause of the negative pressure—the tendency of the surface to contract. Their device of dividing the calculated volumes of liquid by a fractional power of σ, in order to correct for distension, is clearly illogical, for the distension cannot be the same fraction of the volume at all stages of adsorption. At saturation, no distension should occur, and the calculated volumes, without correction, are actually found the same at all temperatures, a fact much stressed by the authors. If the volumes are corrected in the given manner, they will, of course, no longer coincide at saturation.

Clearly the capillary condensation theory cannot claim among its merits any ability even to approximate the facts of experiment. Such approximation might presumably be secured by introducing suitable *ad hoc* assumptions concerning angle of contact, failure of the liquid completely to fill the pores, delay in reaching equilibrium, or the like; but by these means any other theory could be equally well established. It seems to me more reasonable to conclude that the principal cause of adsorption lies not in the surface forces of the liquid itself, but in another class of forces, less influenced by temperature changes and more by the specific nature of the components of the system. This brings us to the second, or adhesion hypothesis, according to which every adsorbed molecule, including those about to evaporate from the liquid surface, is under the direct influence of the adsorbent. The theory has been extensively developed by Polanyi.[6] He assumes that the force upon each adsorbed molecule is specific as to the chemical nature of the molecule, but otherwise depends only upon its position relative to the adsorbent, and neither upon the temperature nor upon the proximity of other adsorbed molecules. The adsorbed liquid obeys its ordinary equation of state; it has its normal density at the surface layer, whether the system is saturated or not, and inferior layers are denser by reason of the compression due to the "weight" of those above. The adsorption space can be considered as the seat of a field of force, the potential of which at each point is the work which the adsorbent does upon a molecule moving to this point from infinity. The surface layer being normal, this potential is to be calculated as before by the equation $\varphi = -k\ T\ ln\ P$, P being now the relative pressure observed when the system has been brought to that degree of saturation which causes the surface of adsorbed liquid to pass through the point in question. Actually there is no method of recognizing particular points in the adsorption space. However, at a given degree of saturation, all points in the liquid surface must have the same potential, which can therefore be considered as a function solely of the volume enclosed between this surface and that of the adsorbent itself. What the nature of this function should be is not predicted by the theory. It can, however, be empirically determined from a single isotherm, the volumes being estimated in the first instance by assuming the normal liquid density. (A better approximation can be made.) The function will evidently have the same form as Curve 1, Fig. 1, with suitable changes of scale. The potential will be found to vanish at a definite volume, with a finite derivative with respect to the volume.

Now, at first sight, this seems impossible. No force is known which acts between two bodies according to such a law that its potential vanishes at a finite distance and with a finite space derivative. All known potentials vanish asymptotically at infinity. If the surface of the adsorbent is nearly plane, the volume of liquid adsorbed should be roughly proportional to the distance separating its surface from the adsorbent, and the potential at its surface should be an asymptotically vanishing function of its volume. But if the adsorbing surface is sharply concave, the volume will itself be a rapidly converging function of the distance, and the ratio of potential to volume may be always finite.

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[6] Polanyi, *Verh. deut. Phys. Ges.*, **18**, 55 (1916).

By way of example, let us calculate the potential as a function of the volume, in the particular case of a spherical cavity of radius A, every molecule within which is attracted by each element $d^2\omega$ of the wall surface with a force d^2F inversely proportional to the cube of the distance. In Fig. 2, M represents the position of the molecule, N is any point of the wall, and S, X, M, L, are distances as indicated. Let the attraction of N for the molecule at M be $d^2F = k\mathrm{S}^{-3}d^2\omega$.

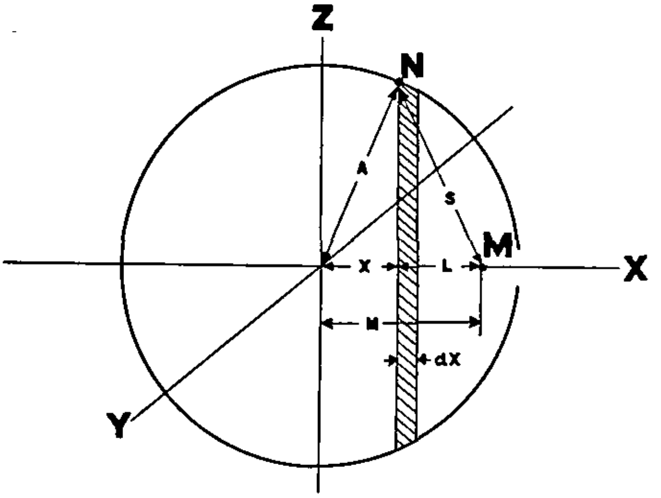

Fig. 2.

Owing to the symmetry of the figure, only the x-component of this force will contribute to the ultimate result. Let this be $d^2F_x = k\mathrm{L}\mathrm{S}^{-4}d^2\omega$. In the figure, the shaded band represents an annular element of wall surface, including N, bounded by the intersections of the planes $X = \mathrm{x}$, and $X = \mathrm{x} + \mathrm{dx}$, and possessing the area $\mathrm{d}\omega = 2\pi\mathrm{A}\mathrm{dx}$. Its attraction for the molecule will evidently be $\mathrm{d}F_x = k\mathrm{L}\mathrm{S}^{-4}\mathrm{d}\omega = 2\pi\mathrm{A}k\mathrm{L}\mathrm{S}^{-4}\mathrm{dx}$.

The potential at M is the sum of the elements of potential contributed by all the annular elements of wall surface, each of which is to be found by integrating the attraction by the distance, from infinity to M. (The molecule is supposed to enter the cavity along the X-axis through narrow channel, too small to prevent treating the wall as a perfect sphere.) For the element $\mathrm{d}\omega$ of potential contributed by the wall element containing N, we find (noting that $\mathrm{S}^2 = \mathrm{L}^2 + \mathrm{A}^2 - \mathrm{X}^2 = \mathrm{M}^2 + \mathrm{A}^2 - 2\mathrm{MX}$):

$$\mathrm{d}\varphi = 2\pi\mathrm{A}k\mathrm{dx}\int_{\infty}^{\mathrm{L}} \frac{\mathrm{L}\,\mathrm{dL}}{(\mathrm{L}^2 + \mathrm{A}^2 - \mathrm{X}^2)^2} = \frac{\pi\mathrm{A}k\mathrm{dx}}{\mathrm{L}^2 + \mathrm{A}^2 - \mathrm{X}^2} = \frac{\pi\mathrm{A}k\mathrm{dx}}{\mathrm{M}^2 + \mathrm{A}^2 - 2\mathrm{MX}}$$

Finally, integrating this with respect to x, from $-\mathrm{A}$ to A, we get for the whole potential

$$\varphi = \frac{\pi\mathrm{A}k}{\mathrm{M}}\, ln\, \frac{\mathrm{A} + \mathrm{M}}{\mathrm{A} - \mathrm{M}} = 2\pi k\left(1 + \frac{\mathrm{M}^2}{3\mathrm{A}^2} + \frac{\mathrm{M}^4}{5\mathrm{A}^4} + \ldots\ldots\right)$$

Now, this is also the potential for all other points whose distance from the center is M. But the locus of these points is a sphere, enclosing between itself and the walls the volume $\frac{4}{3}\pi(A^3-M^3)$. We may, therefore, eliminate the parameter M and obtain the potential as a function of the volume. The function has the form of Curve 2, Fig. 1. (For convenience in computation, the potential and volume have been reduced to abstract numbers by dividing out the dimensional constants; the abscissas are $\varphi/\pi k$ and the ordinates are $100 \times V \times {}^3/_{4\pi A^3}$.) For small adsorption, when $A-M<<A$, the volume may be expressed as $V = 4\pi(A-M)A^2$, and the potential as $\pi k \ ln \dfrac{2A}{A-M}$. Its negative is therefore a linear function of the logarithm of the volume, in agreement with the Freundlich equation for the isotherm.

Other relations between potential and volume, of generally similar character, can be obtained by changing the size or shape of the cavity, or the exponent in the law of force. The latter change will destroy the validity of the Freundlich equation as the limiting case. But this is hardly an objection, since at very low concentrations the presence of liquid is doubtful; the fact that the inverse cube law of force does lead to the Freundlich isotherm is probably a coincidence, and cannot be regarded as proof that it is the correct law.

Curves of the class under consideration differ from observed isotherms in one fundamental respect: they terminate abruptly at finite potentials and volumes, instead of reaching zero potential at finite volumes. Physically, this means that the smallest potential which exists anywhere inside a cavity is greater than zero, since all places within the cavity are under the influence of the walls. Thus, for the case just calculated, the minimum potential (at the center of the sphere) is $2\pi k$, and for any relative pressure corresponding to a lower potential, the cavity will remain completely full. If an inverse fourth-power law be assumed for the same cavity, we get

$$\varphi = \frac{4\pi k A}{3(A^2-M^2)} = \frac{4\pi k}{3A}\left(1 + \frac{M^2}{A^2} + \frac{M^4}{A^4} + \ldots.\right)$$

and the minimum value of the potential is $4\pi k/3A$. Now, an actual adsorbing body should not be supposed to contain cavities of exactly uniform dimensions (with the possible exception of crystalline adsorbents like chabazite). All possible sizes and shapes must be expected to be present. At saturation, they will all be full; as the pressure falls, they will begin to empty successively, each at the moment that the pressure corresponds with its particular minimum potential. The observed isotherm will be a kind of average of the isotherms of all the cavities, and its form will depend upon the manner in which the total volume is distributed among the different kinds of cavities. Since this volume is finite, there must exist a certain volume of single cavity, than which cavities having a greater volume occur much less frequently. As a highly arbitrary, but instructive device, let us suppose that all the cavities are spherical, and so distributed that among the larger cavities their number decreases as the fifth power of their radius, and their combined volume as the square. That is, if dN be the number of cavities having radii between A and $\mathrm{A} + d\mathrm{A}$, then

$$dN = \frac{3n\,d\mathrm{A}}{4\pi\mathrm{A}^5}$$

where n is a constant. Taking the fourth-power law expression for φ, as just given, we find for the *empty* volume of a single cavity corresponding to a given potential, the value

$$V_e = \frac{4}{3}\pi\mathrm{M}^3 = \frac{4\pi\mathrm{A}^3}{3}\left(1 - \frac{4\pi k}{3\varphi\mathrm{A}}\right)^{\frac{3}{2}}$$

The empty volume of all cavities of radius between A and $\mathrm{A} + d\mathrm{A}$ will be $n\left(1 - \frac{4\pi k}{3\varphi\mathrm{A}}\right)^{\frac{3}{2}} \frac{d\mathrm{A}}{\mathrm{A}^2}$, and the total empty volume will be found by integrating this expression from infinity to $\mathrm{A} = 4\pi k/3\varphi$, which is the smallest cavity that will empty at all. The result is $3n\varphi/10\pi k$; in this case, therefore, the isotherm near saturation will be a straight line of finite slope, as observed, continuing to zero potential.

The analysis just presented cannot lay claim to even approximate rigor, since there is no reason to suppose that either the dimensions or the distribution of the cavities in an actual adsorbent are as regular as assumed. However, I believe it is useful as showing that it is not impossible to reconcile the discontinuity observed at saturation, with the hypothesis that the adsorbed vapor is present in the liquid state, without assuming the presence of forces acting as discontinuous functions of the distance. The effect is rather to be ascribed to a discontinuity in the relationship between space available for adsorption, and proximity to the adsorbent surface. The fact that the discontinuity at saturation is not absolutely sudden, may perhaps be explained as due to the action of the outside, plane or convex, surface of the granules of adsorbent. The isotherm of such a surface should show no saturation, but should approach asymptotically the vapor-pressure line of the liquid, as indicated by the dashed line in Fig. 1. But the outside surface is so small in comparison with the interior, that its contribution to the whole isotherm would be recognizable, if at all, only as a correction term. There is some evidence that this correction term becomes more important when the convex surface is increased by powdering the adsorbent. Thus, Gustaver[7] and Williams[8] report more transition curvature at saturation than my curves display. Gustaver worked with powdered charcoal; Williams does not give the state of his charcoal. On the other hand, Lowry and Hulett[9] reduced their charcoal to 0.001 mm. without producing transition curvature.

[7] Gustaver, *Kolloidchem. Beihefte*, **15,** 185 (1922).

[8] Williams, *Proc. Roy. Soc. Edinburgh*, **37,** 161 (1917).

[9] Lowry and Hulett, THIS JOURNAL, **42,** 1411 (1920).

It remains to discuss the effects of temperature on adsorption. This is most conveniently studied by plotting isosteres, or vapor-pressure curves of systems of constant composition. If log p (actual, not relative pressure) is plotted against reciprocal temperature, almost perfectly straight lines are obtained. If the equation of Clausius and Clapeyron is applicable, the negative slope of these lines is proportional to the heat of adsorption. I can see no reason to doubt the validity of this principle. The fact that the condensed phase is capable of varying its composition is no obstacle, for the Clausius-Clapeyron equation unquestionably applies to solutions which are thermodynamically indistinguishable from adsorptions. Nevertheless, doubt and confusion appear to exist, whether and under what condition the principle may be extended to adsorption systems, and a brief discussion seems relevant.

Freundlich[10] states that it is applicable in case the heat of adsorption is measured under such circumstances that the amount adsorbed is practically unchanged. Williams[11] points out the difficulty in conceiving a "heat of adsorption" when nothing is adsorbed. The heat required to elevate the temperature of the system, while the pressure is so adjusted as to prevent any change in composition, is evidently merely a specific heat. In the same paper, "following Donnan in an unpublished paper," Williams advances the idea that the Clausius-Clapeyron equation should hold for heats measured isothermally and under equilibrium pressure, provided the adsorbent does not change its surface during the adsorption. In comparing the heat measurements of Titoff[12] with the heats calculated from the same experimenter's isotherms, he finds the former systematically greater. A part of the discrepancy, Williams believes, is due to the fact that the gas entered Titoff's calorimeter at greater than equilibrium pressure. A residual discrepancy appears to him as proof that the charcoal surface increases during adsorption, evolving a quantity of heat not taken account of by the Clausius-Clapeyron equation. This increase is conceived as strictly reversible, and the energy change involved must be added.

In this reasoning I am unable to concur. No condition is involved in the proof of the Clausius-Clapeyron equation which is not admirably met by a charcoal-vapor system, as the following analysis will show. Let us postulate a thermodynamic system the state of which is completely defined when two variables, which may be chosen as pressure and temperature, are given. Then, for any reversible infinitesimal displacement the increase in the energy of the system will be $\mathrm{d}E = T\mathrm{d}S - p\mathrm{d}V$, where $\mathrm{d}S$ is the entropy increase and p is the external pressure. At the same time, any kind of internal change, including a change of surface, may occur.

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[10] Freundlich "Kapillarchemie," 3rd ed., p. 181.

[11] Williams, *Proc. Roy. Soc. Edinburgh*, **38**, 23 (1918).

[12] Titoff, *Z. physik. Chem.*, **74**, 641 (1910).

Such changes must be reversible, since otherwise, the system as a whole, would not behave reversibly. They cannot perform any outside work, for if they did, this work would have to take the form of a reaction against some outside generalized force, and the system would be found to be sensitive to changes in this force in addition to pressure and temperature. They are, therefore, of no thermodynamic significance.

By well-known methods we obtain from the last equation the relation

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left(\frac{\partial q}{\partial V}\right)_T$$

in which ∂q is the heat absorbed. This is certainly applicable to the special case of a system consisting of definite masses of charcoal and vapor, the total volume being just greater than that of the charcoal alone, so that the composition of the whole system is essentially that of the adsorption phase. Such a system is found to be completely definable in terms of temperature and pressure. $\left(\frac{\partial p}{\partial T}\right)_V$ *is evidently the slope of the isostere, for constancy* of volume implies constancy in concentration of the adsorption phase. On the other hand, if the volume changes isothermally, vapor will be desorbed in quantity sufficient to fill the new space (the volume change of the adsorption phase during this process may be neglected), and the accompanying heat absorbed will be the heat of adsorption per mole (λ) times the concentration (moles per cc.) of the vapor at the given pressure, which may be taken as equal to p/RT. We therefore obtain the equation

$$\frac{\partial p}{\partial T}\text{ (isosteric)} = p\lambda/RT^2, \text{ or}$$

$$\lambda = RT^2\frac{\partial\, ln\, p}{\partial T} = -R\frac{\partial\, ln\, p}{\partial(1/T)}$$

We conclude that the isosteres should agree with the measured heats in accordance with the usual equation, and that a departure, due to possible changes of adsorbent surface, is no more possible than is a departure, in the case of liquids, due to the various internal processes (ionization, solvation, polymerization, etc.) which may be supposed to take place in them.

To return to the first cause suggested by Williams as partly responsible for the observed discrepancies, it must be admitted that heats of adsorption are not measured reversibly. The gas enters the calorimeter at an unknown pressure, higher than that of equilibrium. Now, the heat of adsorption in the sense defined is the "external" heat; it contains not only the total energy difference between the initial and the final states, but an additional term taking account of the work done by everything outside the calorimeter upon everything within. Since the total energy of a perfect gas is independent of its pressure, the internal energy change during adsorption will not depend upon the initial pressure of the gas, provided that the temperature at which it enters the calorimeter is properly controlled. As for the outside work term, each element of gas dn may be thought of as having the pressure p' at the instant it enters the calorimeter; the work done by the environment will be $p'\mathrm{d}V = p' \frac{\mathrm{d}V}{\mathrm{d}n}\,\mathrm{d}n = RT\,\mathrm{d}n$; and the total work will be simply RTn, whatever may have been the pressure. The observed heat, therefore, will not differ from the true λ.

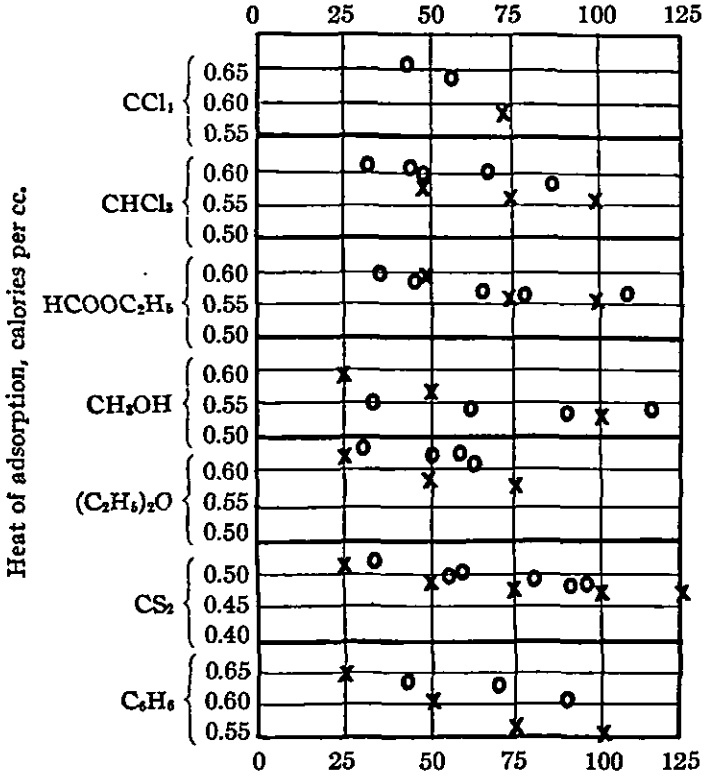

Fig. 3.

It appears, then, that both of the arguments of Williams are thermodynamically unsound, and that the explanation of the excess of measured over calculated heats must be found elsewhere. If things were so arranged that the gas entered the calorimeter with high velocity, its kinetic energy would of course reappear as heat. Calculation shows that with the usual forms of apparatus this effect is negligible. Can the whole difference be laid to experimental error? I think not. The isosteres plotted from my data[4] for organic vapors on charcoal are so regular and extend over so great a range, that it is hard to believe that their slopes are far from correct. In a previous paper[13] in collaboration with A. B. Lamb, I gave direct thermal measurements for many of the same systems, which showed no internal

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[13] Lamb and Coolidge, This Journal, 42, 1146 (1920).

evidence of being as much as one per cent. in error. Fig. 3 shows to what extent the two sets of data are in agreement. Circles show directly measured heats, at average concentrations indicated by the scale of abscissas. Crosses show heats read from the slopes of the isosteres for the indicated concentrations. It will be seen that, as in the data of Titoff, the observed heats generally exceed the calculated, although by a smaller amount. Now, the charcoal used for thermal measurements had been outgassed at 350°, while that used in determining the isotherms had been raised to 550°. This can, however, hardly be the cause of the difference; experiments with benzene and water vapors on differently treated charcoals showed that while the isosteres were slightly shifted, their slopes were unchanged. A more plausible explanation is as follows.

In measuring heats, no special precautions were taken to exclude traces of air. It is known that such traces greatly retard the establishment of equilibrium during the first stages of adsorption, and become less influential as saturation is approached. The ultimate capacity reached is hardly affected. Now, if the first portion of gas is added in the presence of impurities, less heat might be evolved during an hour, say, than if the same amount of pure gas had been used. But when the charcoal is ultimately saturated, the total evolution of heat should be the same, and therefore that observed during the later stages might be greater than normal in the presence of impurities, since it would contain a portion of the heat properly belonging to the first stages, whose appearance had been delayed by the inhibiting effects of the impurities. A discrepancy between observed and theoretical heats, if caused by such conditions, would be negative at low concentrations, zero at some intermediate point, and positive near saturation. Isotherms for low concentrations at 0° cannot be obtained, and comparisons are limited to the later stages of adsorption. Inspection of Fig. 3 shows a marked tendency for the discrepancies to increase with rising concentration, and a rough extrapolation suggests that they might indeed change sign at lower concentrations.

Whatever may be the cause of the discrepancies, the agreement is sufficiently close for a first approximation. Both heat and pressure measurements are evidently entitled to be accepted as free from gross errors, and as furnishing additional confirmation (if any were needed) of the validity of the equation of Clausius and Clapeyron. Furthermore, the slight dependence of the heat of adsorption upon temperature (as evidenced by the straightness of the isosteres) is powerful support for the view stated above, that adsorption does not much depend upon anything with so great a temperature coefficient as surface tension.

The origin of the heat evolved on adsorption has been the subject of discussion. In the paper already cited[13] Professor Lamb and I advanced the idea that it can be regarded as consisting of two parts: first, the ordinary latent heat of condensation of gas to liquid, and second, the heat due to the further action of the adsorbent upon the liquid. The second part, which we termed "net heat of adsorption," alone interested us. A little thermodynamics shows that it bears to the temperature coefficient of the relative pressure, the same relation that the total heat bears to that of the absolute pressure; thus, if l be the net heat, then[14]

$$l = -R\frac{d\, ln\, P}{d(1/T)} = -R\left(\frac{d\, ln\, p}{d(1/T)} - \frac{d\, ln\, p_0}{d(1/T)}\right)$$

where p_m is the vapor pressure of the liquid. Graphically, it is given by the difference in slope between the isostere and the vapor-pressure line of the pure liquid, plotted on the same scale. We found that it is nearly the same in magnitude for different liquids, when referred to equal bulk of liquid, and that the residual differences can apparently be correlated with differences in the total heats of compression which equal volumes of these liquids would evolve when put under a pressure of 37,000 atmospheres, as calculated from the expansion coefficients. Assuming that the attractive forces give rise to a unilateral pressure in the liquid film which causes volume and heat changes equal to those which would be produced by an equal hydrostatic pressure, we came to the conclusion that such high pressures actually exist, and that the net heat of adsorption is merely a heat of compression.

There is apparent confirmation of the high-pressure theory in the work of Harkins and Ewing.[15] They find that the apparent density of certain active charcoals, as determined by immersion in liquids, increases with the compressibility of the liquid used, as though the liquid were highly compressed in the pores. This observation is confirmed by my values for the amounts of different liquids required to saturate my charcoal, and therefore presumably just filling its pores. When reduced to volumes of liquid at normal density, these amounts increase with the compressibility of the liquid, suggesting that the real density of the adsorbed liquid is that corresponding to a high pressure. In so far as the charcoal used by Harkins and Ewing is comparable to mine, the sum of their values for apparent specific volume of charcoal, and of mine for apparent volume adsorbed at saturation, should be constant. How far this is the case will appear from Table I.

However, there are grave obstacles, both theoretical and experimental in nature, which must be overcome before these ideas can be accepted as satisfactory. To consider first the former, we must note that heat of compression, in the thermodynamic sense, is heat evolved when a fluid is compressed by some external agency. It is impossible to apply thermodynamic reasoning to compression caused by internal forces without en-

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[14] This equation was derived by Kirchhoff for the case of solutions, in *Pogg. Ann.*, 104 (1856), Ges. Abh. 492.

[15] Harkins and Ewing, THIS JOURNAL, 43, 1787 (1921).

countering the kind of difficulty which has just been discussed in connection with the theory of Williams. Furthermore, the heat of compression is by no means a measure of the work done by the compressing force, but represents only the difference between the work so performed and the energy retained by the fluid in potential form; it may be positive, negative, or zero. In the case of a liquid attracted to an adsorbing surface, the only outside agency acting upon any given layer of the liquid is the "weight" of the superior layers. That such a "weight" effect exists is apparently indicated by the following experiment, which is typical of the behavior of inorganic liquids, which I am now studying.

To the empty charcoal add a quantity of vapor much less than that necessary to saturate it, and observe the pressure at constant temperature, say 100°. Equilibrium seems to be reached within a few minutes, but if the experiment is prolonged for 20 or 30 hours, a lower pressure will result. Now empty the charcoal and add a much greater quantity of vapor, which will necessitate the use of a lower temperature. Let it settle for a few hours, and then return to 100° and allow the vapor in excess of the amount first used to escape. The pressure will be found to be much lower than even the lowest pressure observed in the first experiment, although the time elapsed has been less. Evidently, the presence of the excess of vapor has accelerated the penetration of the first instalment, presumably by exercising a pressure or "weight" upon it.

If we think of the liquid as being added in successive instalments to the previously bare adsorbing surface, the weight of each instalment, and the consequent increase in pressure upon all previous instalments, will diminish as we get further from the surface, and will vanish when we reach saturation. Now, when a quantity of liquid is compressed, the heat evolved will be proportional to its specific heat of compression, its volume, and the increase in pressure attained. Since no liquid is originally present, the addition of the first instalment can compress nothing and produce no heat of compression. Subsequent instalments will find increasing quantities of liquid available to be compressed, and will, therefore, cause the evolution of increasing quantities of heat of compression, until the point is reached at which the decrease in weight of the successive instalments overbalances the increase in volume of liquid susceptible of compression. If the net heat of adsorption is truly a heat of compression, it should be zero at zero concentration, and rise to a maximum at some higher concentration. Actually, it has its greatest value at zero concentration, and falls continuously with rising concentration; but at saturation it still has a finite value. It must, therefore, contain an additional term, besides heat of compression.

It is not difficult to see what this term must be. When a quantity of liquid "falls" upon a bare adsorbent surface, much potential energy is set free, since the liquid during its approach must be acted on by powerful forces. This energy will be converted into heat, and if the process is isothermal it will be quantitatively transmitted to its surroundings (in addition to that due to the work done by the atmosphere), except that a small portion may be retained if the heat capacity of the system is increased by the process. However, if some liquid is already present, a part of the work done by the adsorbent upon the new liquid will be used in compressing the old, and the heat of compression evolved thereby will not in general be equivalent to the work absorbed. We may expect, therefore, that the observed net heat of adsorption will be closely equal to the work done by the attraction of the adsorbent, only during the initial stages of the adsorption. On the other hand, at saturation the work done (the potential, referred to a mole instead of a single molecule) vanishes, and the net heat of adsorption (heat of wetting) may be regarded as solely heat of compression. This appears paradoxical, for it is hard to see how there could be any compression change at saturation. The difficulty is of the same character as that concerned with the discontinuity in the slope of the isotherm at saturation. If we agree that the potential has a finite derivative at saturation, the proposition may be demonstrated as follows.

Let N_0 be the total number of moles of a given vapor which can be adsorbed by a particular adsorbent at a definite temperature, and let ρ be the reciprocal of the molecular volume of the corresponding liquid at the same temperature and no pressure. Let the molar potential be such a function of the volume not filled by adsorbed liquid, that near saturation $\mathrm{d}\varphi/\mathrm{d}v = K$. When the system is saturated, v is zero, and the potential and the hydrostatic pressure will vanish at the surface of the liquid. At a certain slightly lower surface, the potential will have a value different from zero, namely, $\Delta\varphi = K\Delta v$, Δv being the volume enclosed between the two surfaces; at the same surface the hydrostatic pressure, due to the weight of the intermediate liquid, will have the value $\Delta p = \rho K \Delta v$. Now suppose the intermediate liquid removed; the amount removed will be $\Delta N = \rho\Delta v$. Since the pressure due to this layer is now removed, the remaining liquid will expand by the amount $V_0\beta\rho K\Delta v$, where V_0 is the total volume of adsorbed liquid (supposed large in comparison to Δv), and β is its mean compressibility in the adsorbed condition. The space left empty will be $(1-\rho K\beta V_0)\Delta v$, and a new surface will form at a depth corresponding to the potential $(1-\rho K\beta V_0)K\Delta v$. Recalling the relation between potential and relative pressure, we find for the latter under these conditions, $-RT\ ln\ P = (1-\rho K\beta V_0)K\Delta v$.

Let us now warm the system, without permitting vapor to escape, until it becomes saturated. Let ΔT be the necessary increase in temperature; then, since the new relative pressure is unity, we may write for its mean temperature coefficient over the particular range,

$$\frac{\mathrm{d}\ ln\ P}{\mathrm{d}T} = \frac{ln\ 1 - (-\ ln\ P)}{\Delta T} = K\,\frac{1-\rho K\beta V_0}{RT}\,\frac{\Delta v}{\Delta T}$$

But the reason that the system has become saturated is that the adsorbed liquid has expanded so as to fill the whole adsorption space. If α be its mean coefficient of expansion, this means that $V_0\alpha\Delta T = (1-\rho K\beta V_0)\Delta V$. Eliminating ΔT between these equations, we find $d\, ln\, P/dT = V_0\alpha K/RT$. Therefore, by the analogy to the Clausius-Clapeyron equation, the net heat of adsorption in the immediate vicinity of saturation is $V_0\alpha KT$.

To prove that this is identical with heat of compression, let us return the system to its second, unsaturated state at the original temperature and calculate what heat of compression would be evolved from the liquid present, upon replacing the liquid originally removed. By a well-known thermodynamic relation, the heat of compression of a portion of fluid is proportional to its volume, temperature, and expansion coefficient. Multiplying these quantities by the value of Δp already obtained, we find for the desired heat the expression $V_0\alpha T\rho K\Delta v$. Dividing by ΔN, we obtain for the molar heat $V_0\alpha KT$, a quantity identically equal to the net heat of adsorption just calculated. Here, then, is the explanation of the puzzling fact that the heat required to evaporate a liquid from a saturated adsorbent is greater than from the pure liquid, although the vapor pressures and, therefore, presumably the forces which have to be overcome by escaping molecules, are identical. The additional heat is absorbed by the expansion of the remaining liquid when released from the weight of that which evaporates.

Turning to the experimental field, we find many facts which seem to be inconsistent with the high-pressure theory. The original argument from net heats of adsorption was based on comparisons between different liquids measured at their normal densities. But if they are under high pressure, the quantities chosen for comparison should be those which under high pressure occupy the same volume. This change will alter the results.

The pressure existing in the adsorbed layer, according to Polanyi's theory, is much less than that required to account for the whole heat as heat of compression. It rarely exceeds 5000 atmospheres. The capillary condensation theory denies the existence of any pressure at saturation.

I have previously shown[1] that adsorbed benzene does not freeze, even below its freezing point. If it were in the form of ordinary liquid under pressure, it would freeze at ordinary temperatures.

The most interesting evidence, however, because most closely related to that of Harkins and Ewing, is that obtained by comparing the saturating quantities of the same liquid at different temperatures, rather than of different liquids at the same temperature. McGavack and Patrick's work on silica gel agrees with mine on charcoal in showing that if the decreasing capacity of the adsorbent with rising temperature is due simply to the expansion and overflowing of the adsorbed liquid, then this expansion is about the same as that of the free liquid, and is much greater than that of the liquid under 37,000 atmospheres' pressure. In Table II, the column marked "adsorbed" gives the ratio of the amounts of different vapors adsorbed at the lowest and highest temperatures at which I was able to reach saturation, and the column marked "free" gives the ratios of normal liquid densities at the same temperatures. There is some tendency for the "adsorbed" expansion to be less than the "free," but inspection of Bridgman's[16] work shows that in no case would this correspond to a pressure as high as 500 atmospheres.

TABLE II

EXPANSION OF FREE AND ADSORBED LIQUIDS

Substance	Temp. range, °C.	Adsorbed	Free
Benzene	33–99	1.065	1.09
Ether	0–60	1.09	1.11
Carbon disulfide	0–60	1.07	1.08
Methanol	0–60	1.08	1.07
Water	0–99	1.05	1.04

The case of water is particularly instructive. The expansion of adsorbed water proceeds regularly from 0° to 100°, with no suggestion of a change of sign.

To sum up, then, comparisons between volumes of different liquids adsorbed at one temperature appear to support the high-pressure theory, while those between volumes of one liquid at different temperatures point to the no-pressure or capillary condensation theory. While each of these generalizations has been separately recognized by various authors, the antagonism between them seems to have escaped notice. In order to reconcile the facts, it is necessary to abandon either the idea that all liquids fill the same space, or the idea that every portion of the adsorbed vapor is in a state identical with that of its massive liquid under some particular pressure. I prefer the second alternative for the following reasons.

The properties of a liquid are determined by the forces acting between its molecules. In order to exhibit normal properties, any portion must be surrounded to a distance at least equal to the radius of action of intermolecular forces, by an envelope of similar molecules of the same concentration as exists in the massive liquid. Now I have already given my reasons for believing that every adsorbed molecule (except those at the surface when saturation is reached) is near enough to some portion of the absorbent to be under its direct influence. Unless we are to make the unlikely assumption that the forces between adsorbent and adsorbed molecules have a much greater range than those between adsorbed molecules themselves, this cannot occur unless the adsorbed molecules sacrifice some of their enveloping similar molecules. In other words, the adsorbent should alter the behavior of the adsorbed liquid not only directly by its own attraction, but also indirectly by displacing and removing the attraction of very intimate portions of it. This amounts to dilution, and we are therefore brought

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[16] Bridgman, *Proc. Am. Acad. Arts Sci.*, 49, 1 (1913).

back to Homfray's[17] original point of view, from which an adsorption system appears so intimately mixed as to constitute a single phase—a solution. (Her thermodynamic treatment, however, is erroneous and misleading.) The lowering of the vapor pressure and freezing point, and the suppression of the anomaly in the expansion of water, are in complete accord with this view. Solutions of this class are peculiar in that one component is unable to diffuse, so that the concentration is not uniform throughout, but has all possible values. If the adsorbent be considered the solute, then the concentration will be zero at the surface at saturation, and the surface layer of liquid will be in every way normal; in every other portion, the properties of the liquid will be more or less modified, according to laws which will not be more simple than those applying to ordinary concentrated solutions.

This conclusion will make necessary a revision of the ideas expressed in the first part of this paper, but will not vitiate their general validity. The Polanyi theory must be modified, since we can no longer grant its fundamental assumption that the liquid obeys its normal equation of state. In particular, the method of calculating the potential from the relative pressure will not do. The true potential will, however, approach the apparent potential thus calculated, as the system approaches saturation and the surface layer becomes normal. The reasoning advanced to explain the finite volume derivative of the true potential at saturation will still serve to make intelligible the corresponding finite, but different, derivative of the apparent potential, and therefore of the observed isotherm. The interpretations of heat of wetting as heat of compression, need not be altered, since no assumption was made concerning the state of the liquid save that the surface layer is normal at saturation.

It remains to find an explanation of the fact that observed net heats of adsorption do run parallel to heats of compression—that is, to expansion coefficients. The latter are approximately inverse measures of the work which has to be done in separating molecules of different liquids. We have just seen that such separation probably occurs during adsorption. The necessary work must be subtracted from the direct work done by adsorbent on the individual adsorbed molecules, in calculating the total energy change or the net heat, which would, therefore, tend to decrease, as observed, with decreasing expansion coefficient. This is well illustrated by the case of water, with its very low expansion coefficient, high surface tension, etc. The net heat of adsorption of water, calculated from the isosteres under such conditions as to be comparable with those previously given (1 cc. of liquid on 10 g. of charcoal, as in Col. 5, Table VIII of the Lamb and Coolidge article[18]) is only about 22 calories, while the average for the organic liquids was 88 calories. Mercury is not adsorbed at all. This is presumably not

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[17] Homfray, *Z. physik. Chem.*, 74, 129 (1910).

[18] Ref. 13, p. 1164.

because there is no attraction between carbon and mercury atoms, but because this attraction is insufficient to separate the mercury atoms from each other. Similar considerations might be invoked to explain the differences in the adsorbabilities of other liquids. Portions of the adsorption volume might be supposed to be accessible only to single molecules of liquids like ether, which are easily able to detach themselves from their fellows. Speculations of this nature would best be postponed until data are at hand covering, for a single adsorbent, liquids with a wider range of properties. On the accumulation of such data I am actively engaged.

Summary

Adsorption isotherms are observed to exhibit changes of slope at saturation so sharp as to suggest the appearance of a new phase. This interpretation is at variance with most theories of adsorption, and another is to be desired.

The "capillary condensation" theory is examined and found quite inadequate to account for the facts except with the aid of *ad hoc* assumptions. In particular, it predicts temperature coefficients much greater than those observed. It must, therefore, be supposed that all adsorbed molecules are directly attracted by the adsorbent.

The conditions are discussed under which the action of forces which are continuous functions of the distance can nevertheless give rise to potentials which are discontinuous functions of the volume occupied by the adsorbed gas, thus explaining the observed breaks in the isotherms at saturation.

The relation between heats of adsorption and slopes of the isosteres is discussed. Published objections to the application of the equation of Clausius and Clapeyron are examined and found invalid. The equation is tested by experimental data, and found to be satisfied within a few per cent.; an explanation of the residual discrepancy is offered.

The origin of the heat of adsorption is discussed. It is concluded that the earlier conception of this heat as heat of compression, is in general erroneous, but may be correct for a saturated system. For unsaturated systems, the heat is to be considered as principally representing the work done by the attraction of the adsorbent, plus the ordinary latent heat of condensation.

The evidence for and against the existence of a high pressure due to adsorption is examined. The evidence is found incapable of being reconciled with the idea that the adsorbed liquid obeys its ordinary equation of state. It is concluded that the liquid must be thought of as fundamentally altered in state, as in the case of ordinary solutions. The advantages of treating adsorption as a special kind of solution are discussed.

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[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY OF WESTERN RESERVE UNIVERSITY]

THE DETERMINATION OF TRACES OF MERCURY
II. THE QUANTITATIVE DETERMINATION OF MERCURY IN THE PRESENCE OF ORGANIC MATTER[1,2,3]

BY HAROLD SIMMONS BOOTH, NORA E. SCHREIBER AND KARL G. ZWICK

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Experimental Part

The object of this investigation was to develop an accurate method for the determination of small amounts of mercury in physiological fluids. Practically all the methods for the determination of traces of mercury in the presence of organic matter include the following operations: (1) oxidation of the organic material; (2) concentration of the mercury; (3) separation of the mercury precipitate from the solution; (4) solution of the collected mercury compound; (5) quantitative determination of the mercury.

Oxidation of the Organic Material.—Although the Fresenius-Babo method of oxidation with hydrochloric acid and potassium chlorate has been most widely used, it was thought desirable to avoid the formation of the volatile mercury halides which this produces. A method introduced by Palme[4] and Lomholt and Christiansen,[5] whereby oxidation is effected by means of potassium permanganate in the presence of sulfuric acid, was therefore adopted with a few modifications.[6] In heating to effect oxidation, an all-glass refluxing apparatus (Fig. 1) with a 3-liter, long-neck, round-bottom, Pyrex flask was employed. This prevents losses due to the action on the cork, or other sealing materials, and completely condenses all mercury vapors before they reach the mouth of the flask.

Lomholt and Christiansen[5] first added potassium permanganate to the

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[1] This research was carried out in collaboration with Dr. T. Sollmann and Dr. H. N. Cole of the School of Medicine of Western Reserve University, as a preliminary to a comprehensive study of the absorption and elimination of mercury and mercury compounds by the human body.

The expenses were met by Lakeside Hospital, Cleveland, Ohio, and by a grant from the Therapeutic Research Committee of the Council on Pharmacy and Chemistry of the American Medical Association.

[2] Presented at the Washington Meeting of the American Chemical Society, April, 1924.

[3] For Part I, see THIS JOURNAL, 47, 2625 (1925).

[4] Palme, *Z. physiol. Chem.*, 89, 345 (1914).

[5] Lomholt and Christiansen, *Biochem. Z.*, 81, 356 (1917).

[6] For the study of the oxidation of organic material, solutions containing 1% of gelatin—to simulate the organic matter in urine—to which known amounts of mercury salts were added were used, rather than urine, in order to eliminate in this first study possible interferences which might make it more difficult to evaluate the method. We may add, however, that we subsequently confirmed the method on specimens of urine.

urine, and then concd. sulfuric acid. This causes a great deal of bumping and foaming, which we found could be prevented by adding the sulfuric acid first, heating the mixture to boiling, cooling slightly and then adding the potassium permanganate in 1g. tablets (compressed without a filler) as may be required. Too large an excess of permanganate should be avoided. The mixture is boiled and the oxidation continued until no more organic odors are evolved. The small amount of manganese dioxide which settles out is reduced by the cautious addition of a few drops of "50 volume" hydrogen peroxide, and remains in solution as sulfate. The boiling is then continued for a short time to break down any excess of hydrogen peroxide, which later would oxidize the hydrogen sulfide and liberate free sulfur. Hydrogen peroxide was added rather than oxalic acid because the latter tends to form the insoluble manganese oxalate, which interferes with the later procedure. After the manganese dioxide has been reduced, the condenser is carefully rinsed into the flask, and the clear solution cooled, filtered and transferred to a large beaker for concentration.

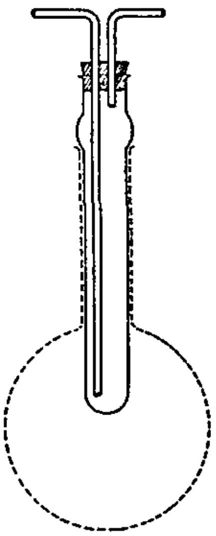

Fig. 1.

Concentration of the Mercury.—Experiment showed that solutions of mercury salts cannot be sufficiently concentrated by evaporation without a partial loss of mercury, nor can all the mercury be volatilized as chloride from the solution even at a high temperature and with a large excess of hydrogen chloride gas present. This precludes the use of evaporation as a method of concentration.

The amalgamation method, according to many investigators, does not give a quantitative separation so that it did not seem worth while to study this method. The precipitation method presented the greatest possibilities for concentration of the mercury, but it was found that with such a small amount of mercury present the sulfide remained in suspension and was difficult to collect on a filter. Raaschou,[7] Palme[4] and Lomholt and Christiansen[5] added copper sulfate to the oxidized solution of the mercury salt and precipitated both the copper and mercury as sulfide. Raaschou thought that the copper sulfide functioned merely to increase the volume of the precipitate. However, the evidence from our experimental work on electrometric titrations of solutions of mercury salts indicates that dilute solutions of mercury salts are hydrolyzed and the mercury is present in part as colloidal mercury compounds. Since this colloid is not ionized, it is not probable that hydrogen sulfide would react with it to precipitate it. Obviously, the copper sulfide adsorbs the colloidal mercury compounds, thus removing both ionized and colloidal mercury salts. A more gelatinous

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[7] Raaschou, *Z. anal. Chem.*, 49, 172 (1910).

compound than copper sulfide, such as manganous hydroxide, would be more effective and proportionately less would be required.

To test this, a series of experiments was conducted to learn whether gelatinous manganous hydroxide, which is easily formed from the manganous sulfate present in the oxidized solution, carries down both suspended mercury sulfide and colloidal mercury compounds.

To 250 cc. of a solution of (1) mercuric chloride and (2) mercuric nitrate, containing 50 mg. of mercury per liter, were added 50 cc. of a 2.5% solution of manganous sulfate and 25 cc. of concd. sulfuric acid. No hydrogen sulfide was added in this case. The solution was made slightly alkaline with sodium hydroxide to precipitate the manganous hydroxide, the solution well stirred and 2 cc. of a 1% sodium hydroxide solution was floated on top. When the manganous hydroxide had settled, the solution was filtered and the filtrate tested for mercury with the electromicroscopic qualitative test.[8] Large *amounts of mercury were invariably found in the filtrate, showing that the coagulation* method *alone* would not remove completely both the ionized mercury and colloidal mercury compounds. The same experiments on the mercury-manganese solution were then repeated but the ionic mercury was first precipitated as the sulfide in acid solution, and the excess hydrogen sulfide removed by bubbling dust-free air through the solution. *This prevents the formation of sodium sulfide later, which would dissolve the* mercuric sulfide. The solution was made slightly alkaline, as previously described, allowed to settle and then filtered through a Gooch crucible, using an asbestos mat.

No trace of mercury could be found in the filtrate even after concentration at room temperature of 25 cc. to one drop. Thus there was less than one part of mercury in one billion left in the filtrate. From this we concluded that the gelatinous manganous hydroxide in settling had completely removed all of the suspended mercury sulfide as well as colloidal mercury compounds. This confirms our statement that in dilute solutions of mercury salts, there are present both mercury ions and colloidal mercury compounds and furthermore, that no quantitative method that fails to take this into account can be accurate. The details of the analytical procedure adopted are fully described under *Summary of the New Method.*

Separation of the Mercury Precipitate from the Solution.—The precipitated mass obtained as described above is filtered through a Caldwell-Gooch crucible of 50cc. capacity provided with a disk supporting an asbestos mat. The precipitate is washed with distilled water until free from alkali and then dried for 10 to 12 hours at 110° in an electric oven.

Quantitative Determination.—We first tried dissolving the precipitate on the Gooch filter and determining the amount of mercury present by electrometric titration[9] with a standard sodium chloride solution. In every case the results were from 4% to 10% too low, depending upon the age of the mercury solutions.[10] This indicates the presence of a variable

[8] Booth and Schreiber, Ref. 3.

[9] Dutoit et Duboux, "L'Analyse des Vins par Volumetrie Physico-Chimique," R. Rouge et Cie., Éditeurs, Lausanne, 1912.

[10] Our study of the electrometric titration of mercury salts will be published later as a separate article.

amount of un-ionized, colloidal mercury compounds, probably in the form of colloidal oxy salts. Any quantitative method, therefore, that does not provide for the determination of colloidal mercury compounds as well as of ionic mercury will be inadequate.

The simplest and most definite procedure for including the colloidal as well as ionic mercury is dry decomposition of the sulfide with an oxidizing agent. Bouton and Duschak[11] decomposed mercury ores by heating with lime and condensing the volatilized mercury. Although this method is accurate enough for relatively large amounts of mercury, we found, as a result of many experiments in which we tried numerous modifications, such as substituting magnesium or barium oxide for lime with or without the addition of cupric oxide, iron or zinc, that where only traces of mercury are present the method gives inconsistently low results. Preliminary experiments showed that decomposition of the mercuric sulfide by lead chromate,[12] a denser substance and an oxidizing agent also, was more promising and so was accurately tested as follows.

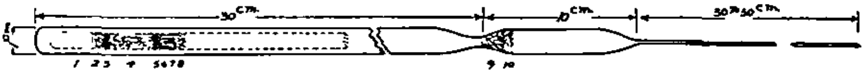

Fig. 2.—(1) Magnesite. (2) Asbestos. (3) Lead chromate. (4) Dried precipitate ground with lead chromate. (5) Lead chromate. (6) Asbestos. (7) Sodium carbonate. (8) Glass wool. (9) Glass wool. (10) Phosphorus pentoxide.

Weighed amounts (0.4–5.0 mg.) of pure mercury were dissolved in a few drops of concd. nitric acid and the solutions diluted. Sulfuric acid and manganous sulfate were added so as to duplicate the oxidized solution. The mercury was then precipitated as sulfide, coagulated, filtered off and dried, as previously described. The precipitate of manganous hydroxide and mercury sulfide was ground in an agate mortar with 0.5 g. of lead chromate, previously dried at 500°. This mixture was transferred to a small glass tube (inner decomposition tube) sealed at one end and containing 0.2 g. of dried magnesite. A loose plug of glass wool was then inserted to keep the mixture in place. It was found necessary to have this small amount of magnesite present in the end of the tube to furnish a small, steady stream of gas to drive the mercury from the decomposed sulfide into the cool portion of the outer decomposition tube. The inner tube was slid into a larger glass tube (outer decomposition tube), Fig. 2, which was then slightly constricted about 10 cm. from the open end. A small plug of glass wool and 0.2 g. of phosphorus pentoxide were inserted to absorb the evolved moisture, which would otherwise prevent the complete collection of the condensed mercury into one globule. The open end was then drawn out to a long capillary. The tube was placed in the decomposition furnace,[12] with the end containing the magnesite projecting from the back of the furnace, and heated for several hours. The tube was then moved forward so that the magnesite would decompose and drive over the last traces of mercury. The portion of the tube projecting from the front of the furnace was cooled with wet wicking, to in-

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[11] Bouton and Duschak, "The Determination of Mercury," *U. S. Dept. Interior Techn. Paper*, 227 (1920).

[12] Zdrahal, *Oesterr. Z.*, 29, 561 (1881).

duce condensation of the mercury which deposited in a narrow band, 4 to 5 cm. from the end of the furnace. The tube was cooled, and broken halfway between the end of the inner decomposition tube and deposit of mercury, and at the constriction. The mercury was then collected into one globule and measured.

The details of this procedure are described under *Summary of the New Method.*

Micrometric Measurement.—On account of the difficulty of completely drying the mercury obtained from the distillation, it is not, in our opinion, advisable to attempt to weigh it directly. It seems more practical and rapid to apply the method of micrometric measurement properly modified, to the accurate determination of this mercury. Raaschou[7] measured the diameter of the mercury globule under the microscope with a micrometer ocular and calculated the weight of the mercury globule. He found, however, that the tendency of the mercury globule to "flatten out" caused an appreciable error in amounts larger than 2 mg.

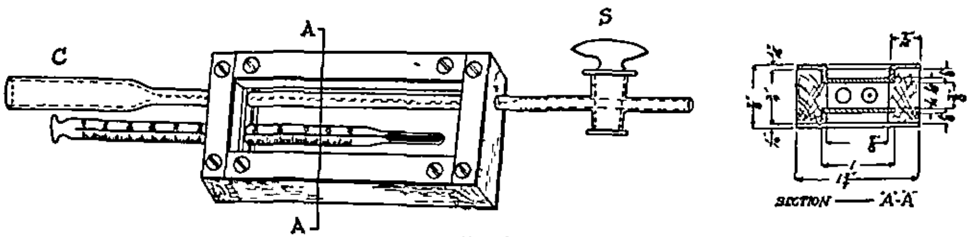

Fig. 3.

It occurred to us that this difficulty might be overcome by transferring the globule of mercury to a fine capillary and measuring the length of the thread of mercury. A piece of capillary tubing about 50 cm. long and of 0.272mm bore, which appeared uniform, was selected. A globule of mercury was drawn into the tubing about 4 cm. from one end, and its length measured with a calibrated cathetometer. The mercury globule was then drawn a few millimeters further along the tube and the length again measured. This was continued until a 10cm. section of uniform bore was found. To one end of this capillary was sealed a capillary stopcock (S), Fig. 3, and to the other, a short piece of glass tubing (C) (8 mm. internal diameter) to guide the globule of mercury into the capillary. This capillary buret was filled with constant-boiling hydrochloric acid[13] and all air bubbles were removed. The globule of mercury was transferred to the small cup (C), the stopcock (S) opened and the mercury drawn down to the middle of the capillary. The stopcock was closed, the excess of acid removed from the cup, and the length of the mercury thread measured with a com-

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[13] Constant-boiling hydrochloric acid is used because this concentration is easily arrived at and maintained, and it was found that the mercury globule would slide down the capillary more easily in hydrochloric acid than in air or water. The hydrochloric acid also removes any foreign substances that have adhered to the surface of the mercury.

parator.[14] With this instrument the end of one meniscus can be brought into line with the cross hairs at the optic axis (care being taken to avoid backlash), the reading taken on the millimeter scale and Vernier, and the body tube slowly moved across the length of mercury until the end of the other meniscus coincides with the cross hairs, and the reading again taken.

The thick glass capillary tubing, however, served as a cylindrical lens, giving a distorted image of the mercury thread and making accurate reading impossible. This lens effect was obviated by immersing the capillary in a medium of the same refractive index as glass, the whole contained in a glass box so constructed that the upper and lower sides would be in parallel planes. The case (Fig. 3) placed horizontally with the capillary buret and thermometer in position, was filled with pale yellow Canada balsam and the cover slide slowly lowered into place to avoid the inclusion of air bubbles. After the balsam had hardened, the brass strips which hold the top glass slide firmly in place were tightly screwed down. Optically, the resulting effect is the same as if a capillary tube were in the center of a glass slab with parallel faces. This device completely eliminates the optical distortion obtained with the capillary tube alone, and at the same time serves to maintain the mercury at a constant temperature in the tube. The resulting mercury thread as seen through the comparator has a convex end, extremely clean-cut, easily observed and measured. According to Kohlrausch[15] and Lohenstein,[16] the mercury meniscus under these conditions is not a hemisphere and the height of the meniscus is so small it is almost negligible. The simplest method of measurement, therefore, seemed to be to plot the weight of a globule of mercury against the length of the mercury thread as measured in the microburet.

Calibration of Microburet and Method of Use.—Various amounts of mercury (0.3 mg. to 6.2 mg.) which had been purified by vacuum distillation, were carefully weighed on a Rueprecht precision balance by methods of substitution and swings. The mercury globule was transferred to the capillary buret in the viewing case, the temperature observed and the length of the column measured.

From the formula $L_0 = L_T/(\alpha T + 1)$, the length of the thread of mercury was corrected to 0° where L_0 is the length of mercury thread at 0°,

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[14] A comparator with a fixed stage and traveling body tube, rather than an ocular micrometer, is required for greater accuracy. With this instrument, measurements are made only in the center of the field, thus eliminating the optical errors possible in the outer edges of the field in an ocular micrometer. It is also possible to measure accurately a longer thread than with an ocular micrometer. The Model M1200 Special, supplied by Gaertner and Co., Chicago, was found satisfactory for this purpose.

[15] Kohlrausch, "Lehrbuch der praktischen Physik," p. 104, Teubner, Leipzig and Berlin, 1905.

[16] Lohenstein, *Ann. Physik*, 33, 296 (1910).

L_T is the length of mercury thread at $T°$ and α is the coefficient of expansion of mercury (0.0001815—Regnault).

The weights of mercury were plotted as abscissas and the corresponding lengths at 0° as ordinates, and a curve was drawn through the points. After such a straight-line graph is plotted, only the length of the mercury thread need be measured, corrected to 0°, and then the corresponding weight may be read directly from the graph. After one becomes familiar with the manipulation there is no difficulty in obtaining an accuracy of 0.01 mg.

Test of the Complete Method.—After the individual parts of the method had been carefully tested, it was thought advisable to run a series of complete analyses, using various quantities of mercury. In order to simulate the actual conditions met with in analyzing urine, feces and other physiological materials, samples of mercury, accurately measured in the capillary buret were dissolved in nitric acid, the solutions diluted to one liter and gelatin was added in various amounts. Since the accuracy of this method of measurement of mercury had been proved, it was thought advisable to measure the sample and final weight of product in the same manner. These solutions were then put through the whole analytical procedure. The result of ten analyses made after this fashion, using amounts of mercury varying from 4.21 mg. to 0.27 mg., are recorded in Table I.

TABLE I

TEST OF COMPLETE METHOD USING SOLUTIONS OF MERCURIC NITRATE AND GELATIN

Length of mercury taken, corr. to 0°, mm.	Calcd. wt. of mercury taken, mg.	Length of mercury found, corr. to 0°, mm.	Calcd. wt. of mercury found, mg.	Error, mg.
0.348	0.27	0.358	0.28	+0.01
0.398	0.30	0.375	0.29	− .01
1.210	0.95	1.158	0.92	− .03
1.651	1.30	1.623	1.28	− .02
2.407	1.89	2.376	1.88	− .01
2.814	2.21	2.780	2.19	− .02
2.844	2.25	2.803	2.22	− .03
3.880	3.08	3.859	3.06	− .02
4.267	3.39	4.244	3.37	− .02
5.341	4.21	5.317	4.19	− .02

The "error" is seen to consist (with a single exception) in a loss of 0.01 to 0.03 mg., with a median of 0.02 mg., and this is independent of the amount taken. It would, therefore, be justifiable to correct the analytical results by increasing them by 0.02 mg., but as the error constitutes only 2% of 1 mg., or 0.4% of 5 mg., we prefer to use the uncorrected values.

Summary of the New Method

One liter of a solution containing a mercury salt in the presence of organic matter is transferred to a 3-liter, round-bottom, long-neck, Pyrex flask; 100 cc. of concd. sulfuric acid is added and the solution boiled for 15 minutes with the internal reflux condenser in place. After the solution has slightly cooled, compressed 1g. tablets of potassium permanganate are added gradually as needed and the mixture is boiled until organic odors are no longer evolved and the solution is clear and colorless. A few drops of 50 volume hydrogen peroxide are added and the solution is boiled until the manganese dioxide is reduced and the excess of hydrogen peroxide decomposed. The condenser is carefully rinsed and removed, the solution cooled and filtered and transferred to a 2-liter beaker.

Hydrogen sulfide is bubbled through the solution for 20 minutes and the excess of hydrogen sulfide removed by bubbling pure, dust-free air through the solution. While the latter is still being slightly agitated with air, a 50% solution of sodium hydroxide is added until a few flocks of manganese hydroxide are formed. These are allowed to settle overnight. The precipitate is filtered on a Caldwell-Gooch crucible fitted with an asbestos mat, washed with water until free from alkali and then dried for ten to twelve hours in an oven at 110°.

The precipitate of mercury sulfide and manganese hydroxide, together with the asbestos, is transferred from the Gooch crucible to an agate mortar and ground thoroughly with 0.5 g. of "*precipitated*" lead chromate, previously dried at 500°. The mixture is transferred through a very small funnel into a glass tube 7 cm. long and 0.6 cm. in diameter (see Fig. 2), sealed at one end and containing in the bottom 0.2 g. of dried, powdered magnesite, then a small layer of asbestos and a 0.2 cm. layer of lead chromate. A small amount of lead chromate is ground in the agate mortar to remove the last traces of the precipitate and this is transferred to the tube above the decomposition mixture. Then a layer of 0.1 g. of dried sodium carbonate is added and the tube is closed with a *loose* plug of glass wool. This tube is placed in a glass tube (36 cm. long) open at both ends, and dried in the tube furnace at 200° for one-half hour. Most of the moisture present is thus condensed in the long, cool portion extending from the front end of the furnace. The small inner tube is then removed through the dry end and slid into a previously dried, outer decomposition tube one end of which is sealed. The decomposition tube is slightly constricted 10 cm. from the open end. A small plug of glass wool is placed outside this constriction and a layer of 0.2 g. of phosphorus pentoxide added. The open end is drawn out to a capillary 30 cm. long. The tubes are placed in the tube furnace with the end containing the magnesite projecting from the back of the furnace. A wicking is wrapped around the outer tube about 2 cm. from the front of the furnace and is kept constantly cool by dripping cold water on it during the decomposition. The tubes are gradually heated to 350° and this temperature maintained for two hours. The furnace is cooled to 200° and the tube moved along so that the end containing the magnesite will be heated and the magnesite decomposed. The temperature is gradually raised to 520–550° and the heating continued for two hours. The tubes are then cooled, the decomposition tube is broken at the constricted part and again half way between the inner tube and the deposit of mercury. This section of tubing is placed in a vacuum desiccator over phosphorus pentoxide and dried for two hours. The deposit of mercury is then collected into one globule with the aid of a slender glass rod, drawn out to a fine hair.

The buret (see Fig. 3) is filled with constant-boiling hydrochloric acid and the globule of mercury transferred to the small cup. The stopcock is opened and the mercury allowed to run down to the middle of the capillary. The stopcock is closed, the excess of hydrochloric acid removed from the cup and the buret placed on the stage of the comparator. The stopcock is opened and when the thread of mercury has come to rest, the length is measured and the temperature observed. The length of mercury is then corrected to 0° by the formula, $L_0 = L_T/(\alpha T + 1)$, and the corresponding weight of mercury read from the graph.

The authors desire to express their appreciation of the kindness of Mr. M. J. Rentschler of the J. H. R. Products Co., Willoughby, Ohio, for furnishing the 50-volume hydrogen peroxide specially prepared so as to be free from interfering impurities.

Summary

1. It is shown that very dilute solutions of mercury salts contain not only mercuric ion but also colloidal mercury compounds and that no method for the quantitative determination of mercury that does not make provisions for the simultaneous determination of ionic mercury and colloidal mercury compounds can be accurate.

2. A method is described which provides for the determination of both ionic and colloidal-mercury compounds and which permits the quantitative determination of small quantities of mercury in the presence of organic matter with a loss of 0.01 mg. to 0.02 mg. of mercury in 5 mg., or less, in a liter of solution.

3. A simplified procedure is given for the oxidation of organic material, which prevents loss of mercury due to volatilization.

4. A new micrometric method for measuring small amounts of metallic mercury is described.

CLEVELAND, OHIO

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

OXIDATIONS IN THE BENZENE SERIES BY GASEOUS OXYGEN
I. OXIDATION OF METHYLBENZENES

BY H. N. STEPHENS

RECEIVED JANUARY 15, 1926 PUBLISHED JULY 6, 1926

The fact that methylbenzenes are oxidized by gaseous oxygen in the presence of moisture and in direct sunlight has been reported by Ciamician and Silber[1] who obtained under these conditions benzoic acid from toluene, the three toluic acids from the corresponding xylenes and cumic acid from cymene. In each case traces of aldehydes were obtained but the quantities were too small for identification. Suida[2] found later that these hydrocarbons, in the presence of water, when exposed to actinic or ultraviolet rays, were oxidized to acids and that part of the oxygen absorbed was activated.

A series of investigations carried out by the writer shows that oxidation of the methylbenzenes by gaseous oxygen also occurs under quite different conditions from those employed by the above-mentioned investigators. The results obtained throw much more light on the course of these reactions. In these experiments dry hydrocarbons were used and oxygen was bubbled through them at elevated temperatures. All oxidations were carried out in dim, diffused light. The hydrocarbons were placed in bulbs sealed to the ends of tall air condensers and into these were inserted small tubes which delivered the oxygen. The temperatures employed were chiefly in the neighborhood of 100°.

In each case the main identifiable product was an aldehyde, and the product occurring in smaller quantity the corresponding acid. This is rather a remarkable fact in view of the reputed ease with which aromatic aldehydes are oxidized. In addition to these two identifiable products there always occurred an appreciable amount of reddish-brown gum, or solid resin, presumably from condensations of the aldehydes.

Although the possibility of alcohol formation as an intermediate stage has not been excluded, in no case examined has the presence of an alcohol been detected in the products. The question of their formation is one which is being further investigated.

Apparently, then, the first recognizable stage in these oxidations results in the formation of aldehydes, and these are later oxidized to the corresponding acids. The "activated" oxygen in Suida's investigations[2] might well be accounted for by the auto-oxidation of the aldehydes[3] although this does not preclude the possibility of intermediate peroxides being formed in earlier stages.

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[1] Ciamician and Silber, *Ber.*, 45, 38 (1912).

[2] Suida, *Monatsh.*, 33, 1255 (1912).

[3] Jorissen, *Chem. Centr.*, 67, II, 964 (1896).

The proportions of aldehyde and acid in the products will be governed by the speeds of the two reactions.

$$RCH_3 + O_2 \longrightarrow RCHO + H_2O \qquad (1)$$

and

$$2RCHO + O_2 \longrightarrow 2RCOOH \qquad (2)$$

The great difference in concentrations of hydrocarbon and aldehyde in the early stages of oxidation will, of course, favor the first reaction but the fact that Ciamician and Silber[1] obtained acids almost exclusively, seems to indicate that an increase of temperature also favors Reaction 1.

Ease of oxidation increases with increasing number of methyl groups, toluene being scarcely affected at 100° and durene being oxidized relatively rapidly. In no case was any product found that would indicate oxidation of more than one methyl group.

The Inhibitory Action of Water.—In carrying out oxidations of this type under water condensers, whereby the water formed by the reaction was caused to accumulate, it was noticed that the speed of reaction diminished. To test further the effect of water on the reactions, mixtures of hydrocarbon and water were treated, at the boiling point, with oxygen. In the cases of *m*-xylene and mesitylene it was found that oxidation was almost entirely inhibited, no aldehyde or acid being detected in either case. This remarkable effect seems to find its simplest explanation in the assumption that, somewhere in the series of reactions that take place, the elements of water are eliminated, and that this reaction is reversible. The study of the action of water is being continued in this Laboratory.

Experimental Part

For the purpose of purification, the hydrocarbons were shaken several times with small amounts of concd. sulfuric acid, washed with sodium hydroxide solution and water and finally fractionated over sodium. Except where specified no attempt was made to dry the oxygen.

The general method of isolating aldehyde and acid was the following. The crude reaction product was distilled under reduced pressure until the boiling point began to rise noticeably, and then the last fraction was distilled into a fresh receiver. This fraction usually contained some acid as well as the aldehyde. Removal of the aldehyde was effected by shaking the mixture with a saturated solution of sodium bisulfite and allowing it to stand for 12 hours or more, when the addition compound was filtered dry and washed several times with ether. The residue of the liquid from which the aldehyde was removed was then washed with water, combined with non-volatile residue from the distillation and treated with sodium bicarbonate solution. Addition of dil. sulfuric acid to this solution yielded the crude acid. Sodium bicarbonate was found to be more satisfactory than sodium carbonate as the latter dissolved or peptized a considerable amount of gummy material. The amount of aldehyde was calculated from the weight of sodium bisulfite compound while the crude acid was weighed directly.

Toluene.—Oxygen bubbled through 100 g. of toluene for 48 days at 100° gave a trace of material which reduced Tollens' reagent, presumably indicating the presence of aldehyde, no acid and a slight residue of gum.

***m*-Xylene.**—Ninety g. of *m*-xylene when treated with oxygen for 30 days at 100° gave 1.9 g. of toluic aldehyde, identified as the phenylhydrazone, m. p. 88–9°,[4] and 0.98 g. of toluic acid, m. p. 110–110.5°.[5]

Action of Water.—One hundred g. of *m*-xylene and 25 cc. of water treated with oxygen for 60 days at the boiling point gave no aldehyde, no acid and only a trace of non-volatile residue.

Mesitylene.—Twenty g. of mesitylene when treated with oxygen for 24 days at 100° gave 0.55 g. of 1,3-dimethyl-benzaldehyde (5), identified as semicarbazone, m. p. 201.5°,[6] and 0.27 g. of mesitylenic acid, m. p. 165.5–166°.[7]

Action of Water.—Fifteen g. of mesitylene and 20 g. of water treated with oxygen for 21 days gave no aldehyde, no acid and a trace of residue.

Durene.—Seventeen g. at 100° when treated with oxygen for nine days gave 0.99 g. of durylic aldehyde identified as semicarbazone, m. p. 241.5°,[8] and 0.84 g. of durylic acid, m. p. 148–149°.[8]

Cymene.—One hundred g. at 85° for 14 days gave 1.23 g. of cumic aldehyde, identified as the semicarbazone, m. p. 201.5°,[9] and 0.81 g. of cumic acid, m. p. 116–116.5°.[10,11]

Summary

1. The oxidation of methylbenzenes by gaseous oxygen has been studied and it has been found that the oxidation proceeds in two recognizable stages, (1) oxidation of hydrocarbon to aldehyde and (2) oxidation of aldehyde to acid.

2. Aldehydes have been identified for the first time in the oxidation of these hydrocarbons by gaseous oxygen.

Minneapolis, Minnesota

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[4] Rudolph, *Ann.*, **248**, 100 (1888); m. p., 87–88 5°.

[5] Jacobsen, *Ber.*, **14**, 2349 (1881); m. p., 110.5°.

[6] Law and Perkin, *Trans. Faraday Soc.*, I Reprint, 1–11 (1904); m. p., 201.5°.

[7] Geuther and Frolich, *Ann.*, **202**, 310 (1880); m. p., 166°.

[8] Auwers and Kockritz, *Ann.*, **352**, 310 (1907); m. p., 243–4°.

[9] Walbaum and Hüthig, *J. prakt. chem.*, [2] **66**, 55 (1902); m. p., 201–2°.

[10] Jacobsen, *Ber.*, **12**, 1516 (1879); m. p., 116–7°.

[11] There was also obtained from cymene a quantity of *p*-tolylmethyl ketone, the production of which will be discussed in a later paper.

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 98]

ELECTRON DISPLACEMENT IN CARBON COMPOUNDS
IV. DERIVATIVES OF BENZENE

BY HOWARD J. LUCAS

RECEIVED MARCH 8, 1926 PUBLISHED JULY 6, 1926

The Lewis theory of molecular structure[1,2] has been of great service in the field of inorganic chemistry. The development of a rational procedure by which the properties of carbon compounds can be related to this theory is one of the pressing problems of organic chemistry. In this paper it will be shown that using the dynamic models of molecules the screening effect[3] of electrons provides a mechanism for the phenomenon of electron displacement[1,4] and that by the application of the principles of electron displacement to the Pauling[5] structure of benzene derivatives it is possible to explain their chemical properties and the phenomena of substitution.

The Screening Effect of Electrons.—We shall accept as self-evident truths the following postulates.

Postulate I. The effective nuclear charge of any atomic nucleus is greatest for the innermost orbit of electrons and least for the outermost orbit.

Postulate II. In any atom the inner electrons act as screens between the nucleus and outer electrons and thus decrease the effective nuclear charge for outer electrons; they are said to exert a screening effect upon the latter.

Postulate III. In any one atom the innermost electrons exert the largest screening effect and the outermost electrons the smallest screening effect.

Postulate IV. The screening effect of an electron in a given shell towards other electrons is not a constant; it is least towards innermost electrons and greatest towards outermost electrons.

These four postulates have been shown to be reasonable theoretically from classical electrostatic considerations, and have been substantiated by physicists in their researches in the field of atomic structure and spectral lines.

The assumption is now made that the relationships which hold between the nucleus of an atom and its electrons also hold between the nucleus of an atom in a compound and the shared electrons in the valence shell of the atom. In order to show how a change in the effective nuclear charge of

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[1] (a) Lewis, THIS JOURNAL, **38,** 762 (1916). (b) "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., **1923.**

[2] Langmuir, THIS JOURNAL, **41,** 868, 1543 (1919); **42,** 274 (1920); *J. Ind. Eng. Chem.*, **12,** 385 (1920); *Nature*, **105,** 261 (1920); *Science*, **54,** 59 (1921).

[3] Sommerfeld, "Atomic Structure and Spectral Lines," Translated by Brose, E. P. Dutton and Co., **1923,** p. 73.

[4] (a) Lucas and Jameson, THIS JOURNAL, **46,** 2478 (1924). (b) Lucas and Moyse, *ibid.*, **47,** 1459 (1925). (c) Lucas, Simpson and Carter, *ibid.*, **47,** 1462 (1925).

[5] Pauling, *ibid.*, **48,** 1132 (1926).

an atom produces electron displacement about other atoms through the mechanism of the screening effect, it is desirable to adopt the view that the shared electrons which constitute a bond are moving in elliptical orbits which inclose the nuclei they join. This is an extension of the Bohr theory of electron orbits and has been made by others.[5,6]

Displacement of Electron Orbits.—Now if in methane, CH_4, one of the hydrogen atoms is replaced by a radical of high electron attraction,[7] R, the orbits joining C to R (Fig. 1) will presumably be pulled out in the direction of R and consequently the electrons will be in the neighborhood of C for a shorter time than they were when the hydrogen atom was present. The pulling away of these orbits from the carbon nucleus leaves it with a larger effective nuclear charge than before, since the more remote average positions of the electrons decrease their screening effect towards the other electrons, a result which follows from Postulate III. Therefore the orbits of the other three electron pairs will be contracted and the electrons drawn more closely to the carbon nucleus. Since the three pairs of orbits are symmetrical with respect to the carbon nucleus, orbital displacement will be distributed equally among them when they all inclose, as in this case, the same other atom.

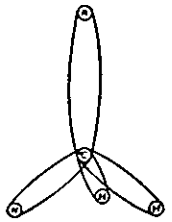

Fig. 1.—Probable enlargement of electron orbits in CH_3R, when R has a high electron attraction.

If the radical has an electron attraction which is less than that of hydrogen the orbits of the electrons which bind it to carbon will be displaced towards the latter with a consequent decrease in its effective nuclear charge. The other three electron pairs will therefore be displaced away from the carbon nucleus.

Displacement of electron orbits is, therefore, a necessary consequence of the extension of the Bohr theory to the shared electron bond. It is evident that this displacement may be transmitted from atom to atom with decreasing intensity, since usually the effect is divided between two or more atoms. The view that in molecules the atoms tend to become alternately polarized[8] cannot be reconciled with the accepted postulates.

In order to indicate relative orbital positions conveniently we shall use

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[6] W. A. Noyes, THIS JOURNAL, 39, 879 (1917). Knorr, *Z. anorg. allgem. Chem.*, 129, 104 (1923). Højendahl, *J. Chem. Soc.*, 125, 1381 (1924).

[7] It is well to distinguish between electron affinity and electron attraction. A substance which tends to appropriate electrons of other substances, and which is therefore an oxidizing agent, may be said to have a high electron affinity. An atom or radical which exerts a strong pull on the shared electron pair joining it to some other atom may be said to have a high electron attraction. Thus, the presence in a molecule of a group possessing high electron attraction may give to the molecule a high electron affinity.

[8] Cuy, THIS JOURNAL, 42, 503 (1920). Hanke and Koessler, *ibid.*, 40, 1726 (1918). Lapworth, *J. Chem. Soc.*, 121, 416 (1922). Kermack and Robinson, *ibid.*, 121, 427 (1922). Allsop and Kenner, *ibid.*, 123, 2296 (1923).

the symbols previously proposed[4c] for static models, namely, o—, -o—, —o-. The small circle in each case represents two electrons, and the circle is placed nearer to an atom the more strongly the electrons are held by that atom.

Electron Displacement in Benzene Derivatives.—In Pauling's model of the benzene molecule (Fig. 2) each closed curve represents a bond which results from the revolving of two electrons in elliptical orbits about the two nuclei of the atoms they join. The electrons constituting the bonds which join each carbon atom to hydrogen and to adjacent carbon atoms move in smaller orbits called λ orbits, and the electrons which join each carbon atom to its *para* carbon atom move in larger orbits called μ orbits.

If now a radical R of high electron attraction (a so-called negative group) such as NO_2 replaces one of the hydrogen atoms of benzene, the resulting electron displacement will be transmitted throughout the molecule and will influence the position of all the other electrons in the molecule. It is proposed to show that the electrons in the C—H bonds suffer different degrees of displacement, and that this difference in degree of electron displacement corresponds to a difference in the degree of reactivity of the *ortho*, *meta* and *para* positions.

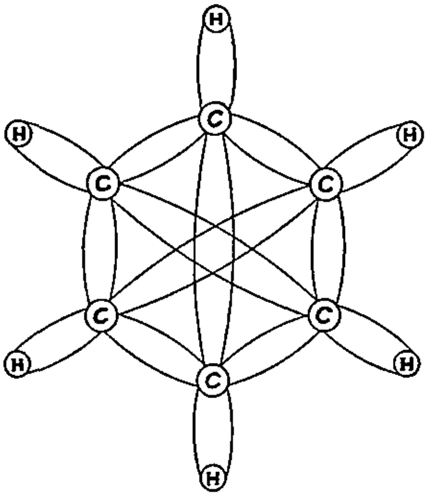

Fig. 2.—The Pauling structure for benzene. Each closed curve represents two electron orbits. The *para* bonds are μ orbits, the others are λ orbits.

Now, in the Pauling formula there is a direct connection to the *ortho* and *para* positions, but not to the *meta*. It is reasonable to infer, then, that any displacement of electrons at the carbon atom C-1 will influence directly the *ortho* and *para* carbon atoms and only indirectly the *meta*. Therefore we may conclude that the *meta carbon will be influenced least by the original electron displacement, and that the ortho and para carbon atoms will be influenced more.*

If Postulate IV is true the substituent group will cause a greater change in the effective nuclear charge of the carbon atom C-1 with respect to μ electrons than with respect to λ electrons, since λ electrons screen the outer μ electrons more than they screen the other λ electrons. Thus the μ electrons are affected more by the substituent group than the λ electrons. On the other hand, the μ electrons are not able to change the effective nuclear charge of a carbon atom with respect to other λ electrons as effectively as λ electrons. Accordingly one is unable to say *a priori* that the *para* carbon atom will be influenced more strongly than an *ortho*, since at the present time we have no quantitative measurements of these phenomena. Now many of the properties of benzene derivatives and most of the phenomena of substitution can be rationally explained if the *para* position is the one which is more strongly influenced; we shall accordingly make that assumption. *In general then the substituent influences the para carbon most, the ortho carbon atoms somewhat less, and the meta carbon atoms least of all.*

Thus the substituted radical R of high electron attraction increases the effective nuclear charges of the carbon atoms of the benzene ring in the order *para* > *ortho* > *meta*. Now the electrons joining these carbon atoms to the hydrogen atoms will be attracted by the former in proportion to the magnitude of these effective nuclear charges, and the magnitudes of these forces are again in the order *para* > *ortho* > *meta*. Fig. 3 shows the relative positions which the electrons or rather the orbits of the electrons have assumed under the influence of the forces now existing in the molecule.

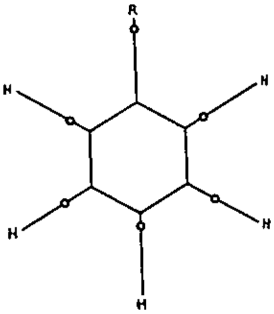

Fig. 3.—Displacement formula for C_6H_5R. This shows the relative positions of the electrons when R has a high electron attraction.

Polarities of the Hydrogen Atoms.—Compared to the hydrogen atoms of benzene, all of the hydrogen atoms in C_6H_5R where R has a high electron attraction are positive, since all of the electrons in C_6H_5R lie closer to the carbon atoms than do those in benzene. The *meta* hydrogen atoms in C_6H_5R are, however, negative in relation to the *ortho* and *para* hydrogen atoms. This may be represented by the polarity formula shown in Fig. 4. This formula should not be interpreted as indicating that the hydrogen in the *meta* position is negative but only that it is less positive than the other hydrogen atoms.

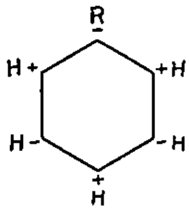

Fig. 4.—Polarity formula corresponding to 3. This indicates that the *meta* hydrogen atoms are the least positive.

Now when a group of low electron attraction (a so-called positive group) such as NH_2 takes the place of a hydrogen atom, electron displacement is towards the ring carbon and is transmitted to the other positions by the mechanism discussed above, with the result that the opposite effect is produced around the ring, in this case the *para* hydrogen being most negative, the *ortho* next and the *meta* least (Fig. 5). Relative to the *ortho* and *para* hydrogens the *meta* is now less negative (Fig. 6), a relationship opposite to that which results when the substituent has a high electron attraction.

It is interesting to point out that Formulas 4 and 6 resemble those proposed by Fry,[9] but with this difference, that whereas the principle of electron displacement demands that nitrobenzene resemble Fig. 4 and aniline

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[9] Fry, "Electron Conception of Valence," Longmans, Green and Co., 1921. Also numerous journal articles.

Fig. 6, Fry assumes that nitrobenzene has the latter structure and aniline the former. However, the displacement Formulas 3 and 5 are much to be preferred to the polarity formulas.

Electron Attraction of Radicals.—It is necessary that we have some means of determining the relative electron attraction of radicals. Many chemists regard NO_2, COOH, and similar groups as negative and NH_2, CH_3, etc., as positive, expressions which, in terms of the theory here presented, mean the possession of electron attractions greater than hydrogen and less than hydrogen, respectively. A strongly negative group usually causes an increase in the ionization constant of an acid and a decrease in that of a base when it is substituted for a hydrogen atom, and a positive group usually brings about the opposite result. There are many groups, however, which produce one effect in one compound, and an opposite effect in another. Such an anomalous behavior is no doubt associated with electrostatic effects operating across space between the substituent and the carboxyl group, a result which may at times outweigh the effect produced by displacement along the chain of atoms. Thus Spiers and Thorpe[10] have shown that the degree of ionization of substituted glutaric acids increases as the carboxyl groups are brought closer together in space.

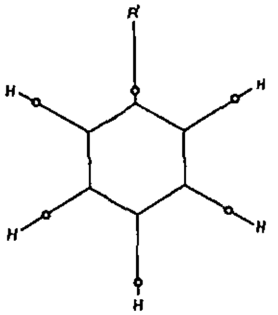

Fig. 5.—Displacement formula for C_6H_5R'. This shows the relative positions of the electrons when R' has a low electron attraction.

In order to obtain a measure of relative electron displacements from data on ionization constants we must select compounds in which the substituents are so far removed that steric influences can be neglected. Since in *para* substituted benzoic acids the carboxyl and the substituent are far apart in space, it seems reasonable to assume that any change in the ionization constant must result from electron displacement, which in turn is presumably proportional to the electron attraction of the substituent. In Table I are listed the ionization constants of some *para* substituted benzoic acids.

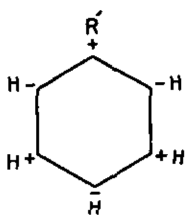

Fig. 6.—Polarity formula corresponding to 5. This indicates that the *meta* hydrogen atoms are the least negative.

The positions of most groups in this table conform to our accepted notions of relative negativity and positivity, since NO_2 causes the largest increase, and NH_2, $NH(CH_3)$ and $N(CH_3)_2$ cause the largest decreases in the ionization constant. The position of hydroxyl is unexpected, since it is usually considered to be negative. However, the positive character of this group becomes more evident when it is noted that the halogens, carboxyl and sulfonic acid increase the electrode potentials of quinol-

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[10] Spiers and Thorpe, *J. Chem. Soc.*, **127**, 538 (1925).

TABLE I

IONIZATION CONSTANTS OF PARA SUBSTITUTED BENZOIC ACIDS[11]

Substituent	NO_2	SO_2NH_2	COOH	Cl	Br	H	$NHCOCH_3$	
$K_A \times 10^5$	40.1	26	13	9.3	6.6	6.6	5.2	
Substituent	OC_2H_5	CH_3	$OCOCH_3$	OCH_3	OH	NH_2	$NH(CH_3)$	$N(CH_3)_2$
$K_A \times 10^5$	5.1	4.5	4.2	3.2	2.9	1.2	0.9	0.9

quinone cells and alkyls, phenyl, methoxyl and hydroxyl decrease the electrode potentials.[12] Now, the *para* bonds are ruptured in the oxidation of quinol to quinone, and the more difficult this process becomes the greater should be the value of the free energy decrease and, therefore, of the electrode potential. The ease with which a *para* bond can be broken should vary inversely with the effective nuclear charges of the ring carbon atoms, and these vary directly with the electron attraction of the substituent. The positive character of hydroxyl is also shown by the fact that the additive power of CO, which is greatest when combined with negative radicals,[13] is much less when it is joined to CH_3, OR, NH_2 and OH.[14]

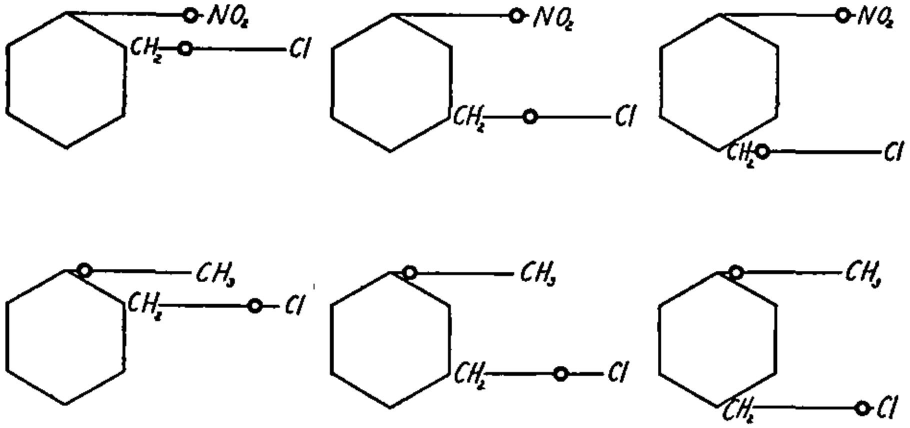

Fig. 7.—Displacement formulas for substituted benzyl chlorides. These show the relative polarities of the chlorine atoms.

Alternation in Reactivity.—The relative reactivities of a group X in $C_6H_4\genfrac{}{}{0pt}{}{R}{CH_2X}$ and $C_6H_4\genfrac{}{}{0pt}{}{R'}{CH_2X}$ can be predicted on the basis of relative electron displacements. Thus if X is Cl, R is NO_2 and R′ is CH_3, the relative polarities of the chlorine atoms are given by the formulas shown in Fig. 7. Since the most negative halogen is hydrolyzed the most easily, the order of hydrolysis rate should be p-CH_3 > o-CH_3 > m-CH_3 > H > m-NO_2 >

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[11] Scudder, "The Electrical Conductivity and Ionization Constants of Organic Compounds," Van Nostrand Co., 1914. The constants of other *para* substituted benzoic acids are now being determined.

[12] Clark, *Chem. Reviews*, 2, 163 (1925).

[13] Stewart, *J. Chem. Soc.*, 87, 186 (1905).

[14] Vorländer, *Ann.*, 341, 9 (1905).

o-NO_2 > p-NO_2. Now this is exactly the order found by Olivier,[15] whose results accordingly strongly support the displacement theory. Likewise chlorine, which is less negative than nitro should produce an effect intermediate between hydrogen and nitro, which it does, although the order is *p*-Cl > *o*-Cl > *m*-Cl instead of *m*-Cl > *o*-Cl > *p*-Cl, as one would predict.

The hypothesis of electron displacement likewise accounts for the relative reaction rates of substituted benzyl bromides,[16] and does so more satisfactorily than the hypothesis of alternate polarity.

Substitution Reactions. μ Electrons not Involved.—Reactions of substitution in the benzene ring are usually brought about by an oxidizing agent such as chlorine, bromine, iodine, nitrous acid, nitric acid, concd. sulfuric acid, etc. It has been pointed out[4c] that in the case of aliphatic hydrocarbons substitution proceeds most rapidly at the point where the attraction of carbon for electrons is least, that is, when the hydrogen atoms are the most negative. In the case of benzene derivatives it is necessary first of all to consider whether the electrons of the outer μ orbits or those of the inner λ orbits are the more easily appropriated by the reagent. It seems reasonable to think that in reactions of substitution a molecule of the reactant must approach close to a molecule of the aromatic compound before it can attract electrons. Now although the μ electrons are in outer orbits as far as the carbon atoms are concerned, it is probable that the reactant cannot approach as closely to them as to the λ orbits which inclose the hydrogen nuclei because the ring of six carbon nuclei would strongly repel the nucleus of any atom except the very lightest when it approached the side of the benzene compound where the μ orbits are exposed, whereas the proton would not exert such a strong repulsion if the reactant should approach the edge where the λ orbits are exposed. Therefore the process of substitution would presumably involve the λ electrons and not the μ electrons.

Since benzene may be converted to cyclohexane by reduction with hydrogen and to hexabromocyclohexane by adding on bromine, it is evident that under favorable conditions the μ electrons may be involved in chemical reactions.

Relative Reactivities of the Ortho, Meta, and Para Positions. Rules of Substitution.—The degree to which a substituting reagent reacts with the λ electrons of a C—H bond depends upon the strength of the attraction exerted upon these electrons by the particular carbon atom. Compared to C_6H_6 these forces are greater in C_6H_5R (R having a high electron attraction) and their strengths are in the order *para* > *ortho* > *meta*,

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[15] Olivier, *Rec. trav. chim.*, 41, 301 (1922).

[16] Lapworth and Shoesmith, *J. Chem. Soc.*, 121, 1391 (1922). Shoesmith, Hetherington and Slater, *ibid.*, 125, 1312 (1924). However, electron displacement does not account for the relative reactivities of nitrochlorobenzenes.

while in C_6H_5R' (R′ having a low electron attraction) they are less and in the order *meta* > *ortho* > *para*. By the deductive method we are led to the following statements.

I. Substitution reactions will, in general, be slower with C_6H_5R than with C_6H_6.

II. Formation of the *meta* isomer will predominate in reactions with C_6H_5R, since the *meta* positions are the most reactive.

III. In the absence of steric effects, the *ortho* isomer will exceed the *para* in reactions with C_6H_5R, since there are two *ortho* positions to one *para* and the *ortho* positions are the more reactive.

IV. Substitution reactions will, in general, be faster with C_6H_5R' than with C_6H_6 and C_6H_5R.

V. Formation of the *ortho* and *para* isomers will predominate over the *meta* in reactions with C_6H_5R' since the *meta* positions are the least reactive.

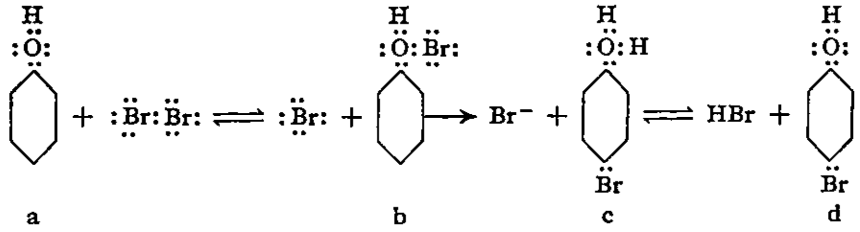
VI. The quantities of the *ortho* and *para* isomers formed in reactions with C_6H_5R' may be almost equal since the one *para* position is more reactive than either of the two *orthos*.

VII. The directive power of a substituent varies in the direction opposite to its electron attraction since, in general, the rate of reaction (upon which the directive power is dependent) itself varies in the direction opposite to the electron attraction of the substituent.

In the main these deductions correctly represent the facts of substitution as they have been elucidated by many workers, especially Holleman and his students. The following exceptions should be noted, however: (a) when R is halogen the main products are *ortho* and *para*, not *meta*, as predicted; this is discussed below; (b) often the amount of *para* exceeds the *ortho* when the *meta* is the main product; this may result from steric hindrance; (c) the directive power does not vary strictly inversely with the electron attraction of the substituent; otherwise, the order would be $NH_2 > OH > CH_3 >$ halogen, whereas according to Holleman it is $OH > NH_2 > Cl > I > Br > CH_3$. But since the directive power of an *ortho-para* substituent is greater than any *meta*, since also in the *meta* directive group the order agrees with the prediction, that is $COOH > SO_3H > NO_2$, and since even in the *ortho-para* directive group the two which exert the strongest directive influence have the lowest electron attraction, it is reasonable to think that there is a fundamental relationship between directive power and electron attraction.

It is instructive to point out here that the *ortho-para* directive power of a group may be decreased by changing hydrogen atoms in the group to radicals of higher electron attraction, and that the *meta* directive power of some other group may be decreased by changing hydrogen atoms in the group to radicals of lower electron attraction. Thus, the *ortho-para* directive CH_3 is changed to the *meta* directive CCl_3 when all of the hydrogens are replaced by the weakly negative chlorine and to the *meta* directive CH_2NO_2 when only one hydrogen is replaced by the strongly negative NO_2. Moreover, the gradual increase in the amount of the *meta* nitro compound resulting from the nitration of the following: $C_6H_5CH_3$ (4.4%), $C_6H_5CH_2Cl$ (4.2%), $C_6H_5CHCl_2$ (33.8%), and $C_6H_5CCl_3$ (64.5%),[17] indicates a gradual and not an abrupt change from *ortho-para* to *meta* directive power. The decrease of *ortho-para* directive power is shown also in the case of *p*-cresol and *p*-cresyl carbonate, the percentages of the 3-nitro compounds resulting from nitration being 100% and 3.7%, respectively. Here the replacing of hydrogen by the negative carbonate decreases the *ortho* directive power, but in this case we must realize that steric effects may be coming into play. An opposite result is observed in the case of benzoic acid and ethyl benzoate, which yield, on nitration, 80% and 68%, respectively, of the *m*-nitro derivative.[17] Here the replacing of hydrogen by the positive ethyl decreases the electron attraction of the entire group so that more of the *ortho* and *para* isomers are formed at the expense of the *meta*.

Substitution Involving Reaction with the Substituent.—Since the substituting reagent tends to acquire electrons, it is possible that it may react with unshared electrons of the substituent already joined to the ring, forming an intermediate compound which can rearrange to yield an *ortho* or *para* derivative. Thus it is conceivable that bromine and phenol may react according to Equation 1 in which one of the bromine atoms, by attracting one or more electrons of the oxygen atom to its shell forms an unstable addition product, from which the second bromine atom drops out as bromide ion. The first bromine atom now joined to the oxygen by a stable bond next exchanges positions with an *ortho* or *para* hydrogen atom of the ring to give a bromophenoloxonium ion. The dropping off of the hydrogen ion to give finally bromophenol and hydrogen bromide may take place as indicated, or may happen earlier in the process. The formation of (b), Equation 1, is analogous to the reaction of bromine with water to form hydrobromic and hypobromous acids and to that of bromine with tribromophenol to form tribromophenyl hypobromite.[18] The rearrangement of (b) to (c) may be ascribed to the well-known tendency of radicals



(1)

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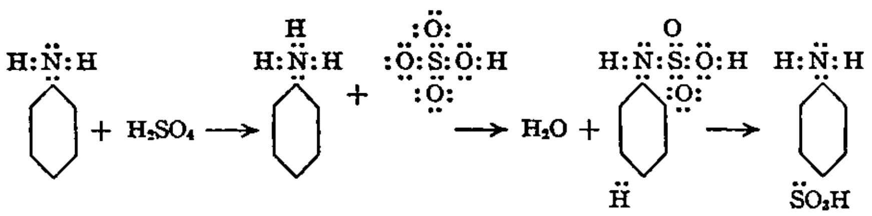
[17] Holleman, *Chem. Reviews*, I, 187 (1924).

[18] (a) Lauer, This Journal, 48, 442 (1926). (b) Benedict, *Ann.*, 199, 127 (1879).

to migrate from oxygen to the ring and is analogous to the rearrangement of tribromophenyl hypobromite to tetrabromophenol.[18b] Since migrations to the *meta* position are comparatively rare, it is evident that they are more difficult to accomplish than those to *ortho* and *para* positions. Thus the movement of bromine from oxygen in the hypobromite to the *meta* position in tetrabromophenol demands such vigorous treatment as heating with concd. sulfuric acid to 118°.

A similar series of changes can be assumed to take place during nitration and sulfonation and with greater justification because in this case the first and last steps are known to take place. When sulfuric acid reacts with aniline (Equation 2) salt formation takes place first with production of the phenyl ammonium and bisulfate ions. When heated, these react by elimination of water to produce phenylsulfamic acid, which is known to rearrange easily, in presence of acid, to aniline sulfonic acids.[19] Similar rearrangements take place in the case of oxygen compounds; thus phenyl hydrogen sulfate easily rearranges to phenolsulfonic acid[20] (Equation 3) and phenyl sodium carbonate to sodium salicylate.



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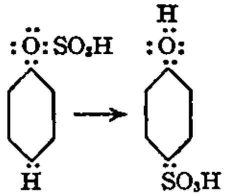

(3)

Numerous other cases are known where radicals migrate to *ortho* and *para* positions from nitrogen and oxygen, and even from halogen.[21] Since in the Pauling structure there is a direct connection to the *ortho* and *para* positions, and none to the *meta*, this model satisfactorily accounts for the position taken.

This type of reaction does not take place unless there are unshared electrons in the shell of the atom which is directly joined to ring carbon. None of the *meta* directive groups contains such electrons.[22] Therefore, although chlorine would ordinarily be expected to direct *meta* from a con-

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[19] Bamberger and others, *Ber.*, 31, 654, 1261, 2277 (1897).

[20] Baumann, *Ber.*, 9, 55, 1715 (1876).

[21] Keppler, *Ber.*, 31, 1136 (1898). Jannasch and others, *Ber.*, 31, 1710, 1714 (1898).

[22] Vorländer [*Ber.*, 58B, 1893 (1925)] has shown recently that —IO_2 and —IC_6H_5-NO_3 are *meta* directive. Here the iodine atoms have unshared electrons.

sideration of its electron attraction, it is probable that its *ortho-para* directive power is due to the tendency of the reagent to appropriate its unshared electrons rather than those of the ring. Such an explanation may in part account for the great difference in the directive influence of NO_2 and NO which are *meta* and *ortho-para* directive, respectively,[23] although the greater electron attraction of NO_2 is an important factor. Also the difference between NH_2 and NH_3^+ (present in salt of amines) which are *ortho-para* and *meta*[24] directive, respectively, may in part be due to the presence of unshared electrons in the NH_2 although here also the relative electron attraction must be considered. The introduction of H^+ into NH_2 would increase the electron attraction of the group as a whole because of the pull exerted by the additional hydrogen nucleus.[25]

That a reaction may proceed by the reagent appropriating unshared electrons on the substituent already present, followed by the migration of a radical to the *ortho* or *para* position, is an assumption which agrees with the views of Karrer[26] in regard to the method by which diazonium salts couple with ethers and with tertiary amines. The splitting off of alkyl groups during these coupling processes necessitates only that the alkyl group instead of hydrogen drop off from the oxygen or nitrogen atom, as the case may be. Since the splitting off of methyl in the reaction of nitrous acid with phenylmethyl ether to produce *p*-nitrosophenol[27] may proceed in the same way, we need no longer consider this reaction as evidence in support of the view that the reagent adds to a double bond of the benzene ring.[28]

The orienting influence of substituents in the benzene ring seems to depend upon two factors, namely, electron attraction and the presence of unshared electrons on the atom joined to ring carbon. If the electron attraction is greater than hydrogen and unshared electrons are absent, the *meta* position is entered; if slightly greater than hydrogen and unshared electrons are present, the *ortho-para* position is entered; if less than hydrogen, the *ortho* and *para* positions are taken whether there are unshared electrons on the atom joined to ring carbon or not. It is significant that the most strongly directive groups contain such electrons.

Summary

The Lewis theory of molecular structure promises much in the way of explaining the chemical properties of carbon compounds. It must be

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[23] Ingold, *J. Chem. Soc.*, **127**, 513 (1925).

[24] Vorländer, *Ber.*, **52B**, 263 (1919).

[25] Compare Latimer and Rodebush, THIS JOURNAL, **42**, 1425 (1920). Lewis, Ref. 1b, p. 141.

[26] Karrer, *Ber.*, **47**, 1275 (1914).

[27] Meyer, *Ann.*, **398**, 80 (1913).

[28] Stieglitz, THIS JOURNAL, **44**, 1304 (1922).

interpreted in the light of physical principles which include the screening effect. By extending the Bohr concept of elliptical orbits to shared electrons it follows that a displacement of an orbit in one part of a molecule causes displacement of the other electron orbits in the same general direction. When these concepts are applied to the Pauling model of benzene, we obtain displacement formulas of benzene derivatives which indicate the relative attractive forces between the carbon nuclei and the electrons in the respective carbon-hydrogen bonds. These formulas account for the relative reactivities of substituted benzyl chlorides and bromides and for the phenomena of substitution.

A measure of the relative electron attractions of radicals is given by the ionization constants of *para* substituted benzoic acids.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 180]

THE ULTRAVIOLET ABSORPTION SPECTRA AND THE PHOTOCHEMICAL DECOMPOSITION OF GASEOUS HYDROGEN BROMIDE AND IODIDE

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The purpose of this investigation was to study the ultraviolet absorption spectra of the hydrogen halides during photochemical decomposition in order to test the validity of two alternative mechanisms which have been suggested to explain the existing experimental facts.

Before the quantum theory of band spectra of molecules had received its great development Warburg[2] suggested the following mechanism, which was in accord with his experimental observations. The absorption of a quantum of ultraviolet light decomposed a single hydrogen halide molecule into atoms which late reacted with another hydrogen halide molecule in such a manner as to produce one hydrogen and halogen molecule. More recently Stern and Volmer,[3] in view of the recent developments on the theory of band spectra have assumed that the absorption of the radiation did not produce direct photochemical decomposition, but that it did produce an excited molecule which would, upon collision with another hydrogen halide molecule produce one hydrogen and halogen molecule. With the aid of the quantum theory of band spectra[4] it is possible to

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[1] From the Doctor's Dissertation of Harold C. Tingey, Massachusetts Institute of Technology.

[2] Warburg, *Sitzb. preuss. Akad. Wiss.*, **1916**, 314; **1918**, 300.

[3] Stern and Volmer, *Z. wiss. Phot.*, **19**, 275 (1920).

[4] Sommerfeld, "Atomic Structure and Spectral Lines," translated from third German Edition by Henry L. Brose. E. P. Dutton and Company, New York, **1923**.

predict the type of absorption spectrum which corresponds to either of the above mechanisms. Thus, a band absorption spectrum would be expected to be found if the Stern and Volmer mechanism were correct. On the other hand, if Warburg's mechanism were true the absorption spectrum would not consist of bands, but would probably be continuous, which is analogous to atomic absorption spectra of similar origin.

The absorption spectra found for pure hydrogen bromide and hydrogen iodide in this research appear continuous. Reasons are given which support the thesis that they are truly continuous and the results are in agreement with Warburg's mechanism.

Experimental Part

Hitherto, a monochromatic light source has been the ideal in exact photochemical experimentation. On the contrary, in this research a source of light which emits a continuous spectrum was necessary to reveal the structure of the absorption spectrum. The experimental procedure consisted in photographing the ultraviolet spectrum of a source of light which emitted a continuous spectrum with and without the interposition of a quartz-absorption tube containing the pure gaseous hydrogen halide.

The Vacuum Line.—This was constructed of Pyrex glass, and was pumped by a mercury diffusion pump, backed up by an oil pump capable of producing a vacuum of 0.001 mm. The McLeod gage read down to 0.00001 mm., and with the pumps going the pressure could be reduced much further.

Sources of Ultraviolet Radiation.—For a reference standard, the cadmium spark spectrum was used. It was excited by high frequency current from a coil for this purpose discharging at about 3000 volts between cadmium electrodes.

For the production of band absorption spectra, a source of continuous ultraviolet radiation is necessary, and it is highly desirable that the intensity should be uniform throughout the range of wave lengths. Good results cannot be obtained with a metal spark spectrum on account of the lines. The source used in these experiments was a hydrogen discharge tube. It was made of 6mm. Pyrex glass tubing, with a polished quartz window 1 mm. thick cemented with de Khotinsky cement on one end. The electrodes were tungsten wire spirals. The tube was filled with dry electrolytic hydrogen at about 15 mm. pressure, the optimum operating pressure being determined by slowly reducing the pressure while the discharge was passing. The current was supplied by the high frequency coil. An intense, striated discharge resulted, blue at first, but changing to pink as the tube became hot.

The radiation from this tube was focused on the spectrograph slit, and the spectrum was continuous and uniform,[5] without lines, for wave lengths

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[5] The intensity fell off in the region 2200–2000 Å.

between 4000 Å. and 2000 Å., the short-wave limit of the spectrograph used. The spectrum showed lines (unidentified) in the visible and near ultraviolet down to 4000 Å., but these did not interfere with the present experiments. The one draw back to this source was that it required exposures of about an hour, compared with one minute for the cadmium spark.

The Spectrograph.—A small Fery spectrograph, manufactured by Ch. Beaudouin, was used. A cylindro-spherical quartz lens throws an elongated image of the source on the slit. Light from the slit enters the prism, is reflected from its curved back, and is thus focused on the photographic plate. Three exposures could be made on one plate. The entire spectrum from 8000 Å. to 1800 Å. was obtained in one exposure, and covered a length of about 8 cm. The plates used were the Eastman Kodak Company Seed's L. Ortho Plates. They were developed in pyro-tank developer at 17° for 30 minutes.

The Absorption Tubes.—Two absorption tubes made entirely of transparent fused quartz were used in the experiments. Both were cylindrical, of 4 cm. diameter. Tube No. 1 was 12 cm. long, and had two side arms, distant about 3 cm. from the ends. Tube No. 2 was 23 cm. long, and had a single side arm near one end. The ends were clear and polished and were about 1 mm. thick. During most of the experiments the side arms were sealed by means of graded seals to Pyrex glass, so that the tubes could be joined directly to the rest of the apparatus without the use of cemented joints. This, together with the all-quartz construction of the tubes, made it possible to evacuate them at high temperatures, thus eliminating absorbed impurities.

Tube No. 3, used in some of the experiments, was a length of Pyrex tubing 90 cm. long and 20 mm. in diameter, with quartz end-windows 1 mm. thick cemented on with de Khotinsky cement.

Preparation and Purification of the Hydrogen Halides.—The hydrogen halides were prepared by dropping 85% orthophosphoric acid, of analytical grade of purity, on the potassium salts (prepared by five recrystallizations of the C. P. product), in the apparatus of Fig. 1. A dropping funnel A is fitted by ground-glass joint B into a 250cc. flask C, which contains the salt. D is a trap to condense water, E a phosphorus pentoxide tube containing a vertical column of this substance about 20 cm. long. The system was evacuated to 0.0001 mm., then orthophosphoric acid (previously boiled) was admitted, and the reaction was started by warming. The hydrogen halide, with some water, passed through D, where most of the water condensed; then through E, where the rest of the water was removed; and finally to the trap F, where it was condensed by liquid air. The 4-liter bulb H, evacuated to 0.0001 mm., was shut off at G during this procedure. When enough material had collected in F, the apparatus was sealed off at J, and the system thoroughly evacuated through I, keeping the hydrogen halide frozen. The stopcock I was then closed, and the gas allowed to evaporate through G into H; the last portion, which contained visible amounts of free halogen, was rejected. In this way a bulb of the hydrogen halide at atmospheric pressure, free from water, and from phosphorus and mercury compounds, was obtained. The freshly prepared material froze to a pure white solid; it melted sharply and at constant pressure; this pressure (as read on a capillary manometer) was within 2 mm. of that calculated from the equations of Henglein[6] for the vapor pressures of hydrogen bromide and iodide. Hydrogen bromide, and to a greater extent hydrogen iodide, decomposed slowly on standing in these bulbs, giving free halogen, which also attacked the stopcock grease. Impurities thus introduced were, however, removed in filling the absorption tubes as described below.

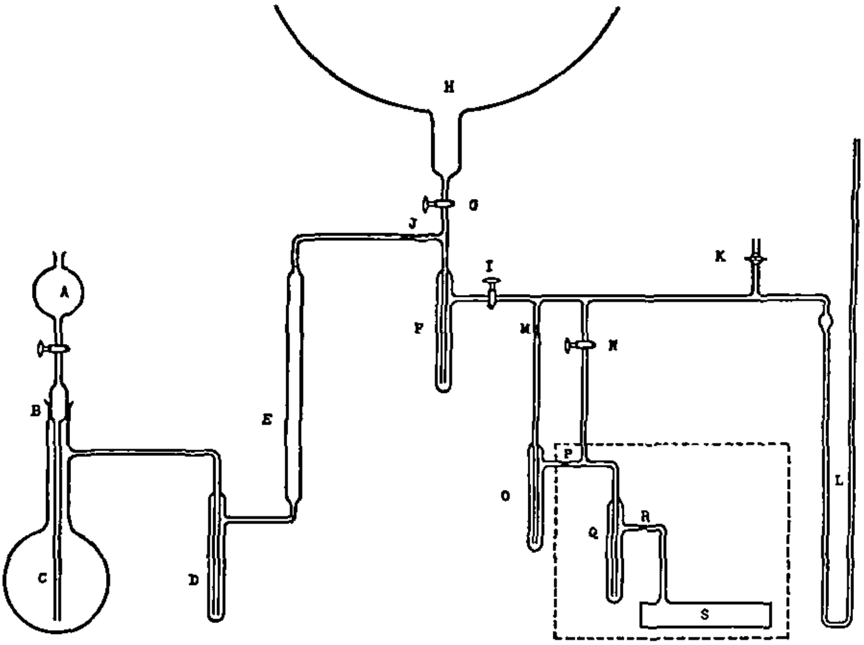

Fig. 1.

Filling the Absorption Tubes.—In the first experiments, hydrogen bromide was led directly from the generator into the absorption tube; spectrographic evidence was obtained of an impurity, and thereafter the gas was purified by distillation as follows.

Referring to Fig. 1, F-G-H-I is the storage bulb previously described; stopcock K affords connection to the vacuum line and McLeod gage; L is a mercury manometer on which pressures from 0 to 2 atm. could be read; O and Q are traps; S is the absorption tube. The portion of the

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[6] Henglein, *Z. Physik*, **18**, 64 (1923).

apparatus inclosed by the dotted lines can be surrounded by an electrically heated oven.

The system was thoroughly pumped out with the stopcock I open; then the oven was heated to 550°, and the pumping continued for an hour at this temperature. During the heating appreciable amounts of gas, consisting mainly but not entirely of water vapor, were given off. During the last half hour, the stopcock N was closed, and the trap O immersed in liquid air. The oven was removed, and the liquid air transferred to trap Q. In this way it is believed that all water and mercury vapors were removed and kept from the tube S. The trap O was sealed off at H and P before it warmed up. Now with the stopcock I closed, all the gas in H was condensed and frozen in F, and allowed to evaporate back into H until the material had melted and boiled for some time. Then G was closed; the material left in F was frozen, and allowed to sublime slowly from F to Q (which was still surrounded by liquid air), until enough had accumulated. Then with I closed the material in Q was evaporated until the desired pressure was reached, when the absorption tube was sealed off at R.

It was found that the baking out had no effect on the spectrum obtained, so this procedure was omitted in most of the experiments except those on the electrical conductivity of the gas. The redistillation, however, was carried out in all cases.

Experimental Results

Absorption of Spectra of HBr and HI.—The tables give the results of the experiments on the absorption of radiation by hydrogen bromide and iodide. The temperature was that of the room except in Expts. 9, 10 and 11 when it was 25°, 250° and 400°, respectively.

In Tables I and II, the time given is the length of exposure; the temperature and pressure are those of the absorbing gas; "Tube No." refers to the absorption tube; "Plate No." identifies the photographic plate; "L" is the length in centimeters of a column of the gas at one atmosphere pressure, equivalent in absorption to the absorbing gas (assuming Beer's law). It is calculated by the equation, L = Pressure/76. The results are arranged in order of increasing "L." The term absorption limit will be made clear below.

The absorption spectra of hydrogen bromide and iodide appeared continuous, showing no evidence of lines or bands. To determine whether our instrument gives high enough resolution to show the separate partial bands of a possible electronic band system, the following calculations were made. The center of the fundamental infra-red band of hydrogen bromide[7] at 3.9μ, is at wave number $v = 2560$, where $v = I$/wave length in cm. Hence the separation of the centers of the partial bands in the ultraviolet band system would be, in wave numbers, approximately $v = 2560$. If L

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[7] Imes, *Astrophys. J.*, 50, 25 (1919).

TABLE I

HYDROGEN BROMIDE

No	Time, min.	Press Cm. of Hg	L	Absorp. limit	Tube No	Plate No.	Notes
1	60	0.9	0.25	2270 Å.	2	28b	4
2	40	4	1.2	2350	2	27c	
3	30	4	1.2	2340	2	28a	4
4	100	2	2.4	2380	3	30c	
5	100	7	8	2430	3	30b	
6	30	37	11	2480	2	26a	
7	65	37	11	2480	2	26b	
8	45	76	12	2460	1	19a	1, 2
9	60	45	13.5	2480	2	38a 39a	5
10	60	45	13.5	2480	2	38b	5
11	60	45	13.5	2480	2	38c 39b	5
12	100	14	16.5	2520	3	30a	
13	100	70	21	2560	2	35a	5
14	90	76	23	2570	2	24a	1, 3
15	100	38	45	2580	3	29c	
16	50	152	46	2520	2	21a	1
17	100	152	46	2520	2	21c	1
18	95	152	46	2600	2	25a	
19	40	152	70	2900	1 and 2	22b	1
20	100	152	70	2800	1 and 2	23b	1
21	100	76	90	2630	3	29a	

TABLE II

HYDROGEN IODIDE

22	100	0.2	0.25	2600 Å.	3	32b	6
23	100	1	1.2	2960	3	32a	6
24	100	20	24	3140	3	31c	6
25	100	43	51	3230	3	31b	6
26	100	120	142	3300	3	31a	6

Notes: 1. Gas not purified by distillation; band spectrum present. 2. Gas was moist. 3. Visible amount of Br_2 present. 4. Absorption limit poorly defined. 5. Absorption tube baked out at 550°. 6. During experiments on HI, a red substance probably HgI_2, formed in tube.

and L' are the wave lengths in centimeters of the centers of two adjacent bands, then $v = (1/L) \times (1/L')$, or $L = L'/(L'V + 1)$. Placing $L' =$ 2500 Å. = 0.000025 cm. (the region in which hydrogen bromide absorbs), the value of L is 2350. That is, the centers of the bands of hydrogen bromide would be separated by 150 Å., or 0.5 cm. on our photographic plates. By a similar calculation it can be shown that the separation of the lines in a partial band would be 1.25 Å. Our instrument would not resolve such lines; but if the lines from two adjacent bands were to merge into a uniform continuous spectrum, each band would have to contain 150/1.25 = 120 lines, of uniform intensity. As this is highly improbable, it appears that hydrogen bromide and iodide have no electronic band absorption spectra.

In the first experiments, a band absorption spectrum was observed extending from 3100 Å. to 2830 Å., approximately, and having 14 flutings in this range. In these experiments the gas was passed over phosphorus pentoxide; the impurity was probably a compound of phosphorus. The fact that this spectrum was eliminated by distilling the gas shows that it was not due to hydrogen bromide. The region of continuous absorption extended from the far ultraviolet (2000 Å.) to a long wave limit, designated as the absorption limit in the table, which depended on the mass of gas traversed by the radiation. This absorption limit was not absolutely sharp, but the transition from apparently complete absorption to apparently complete transmission occurred within a short range of wave lengths (about 30 Å.). The variation of the absorption limit with L can be seen from the tables, and also from the plot in Fig. 2. As the mass of the absorbing gas increases, this limit approaches a limiting value, which is about 2640 Å. for hydrogen bromide and 3320 Å. for hydrogen iodide. These values agree with those found by Coehn and Stuckardt,[8] which were about 2650 Å. for hydrogen bromide and 3340 Å. for hydrogen iodide. Varying the pressure from 0.01 atmosphere to 2 atmospheres has no effect

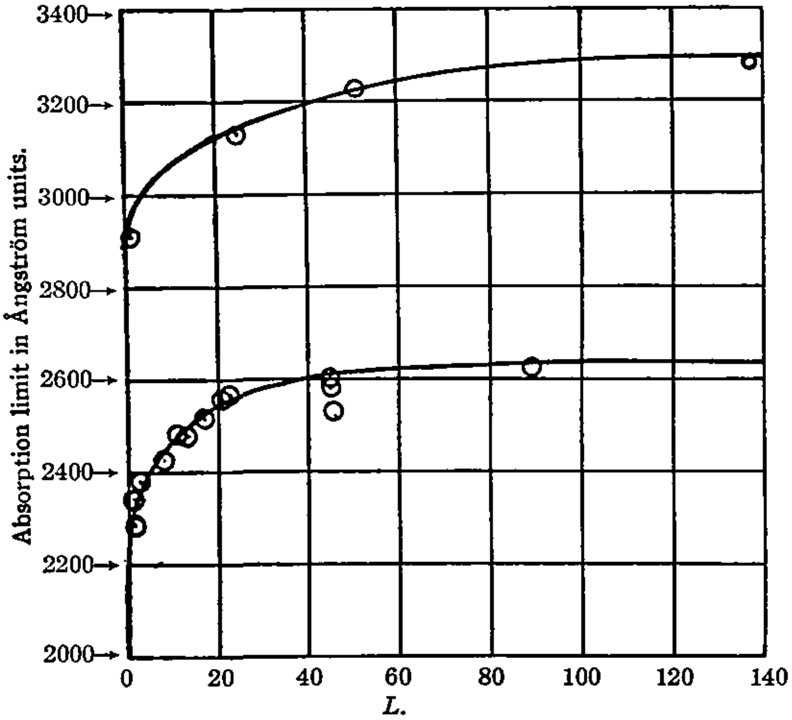

Fig. 2.—Absorption limits and wave lengths.

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[8] Coehn and Stuckardt, *Z. physik. Chem.*, 91, 722 (1916).

on the nature of the spectrum; nor does it affect the absorption limit, as long as L remains the same. (Compare Nos. 7 and 8; 15 and 18 in Table II.) Varying the temperature from 25° to 400° does not affect the nature and intensity of the absorption, or the absorption limit (compare Nos. 9, 10 and 11 in Table II). These observations on the effect of temperature and pressure also confirm those of Coehn and Stuckardt.

Attempts to Excite an Emission Spectrum of Hydrogen Bromide

A tube similar to the hydrogen tube fitted with aluminum electrodes was filled with hydrogen bromide at 1.5 mm. pressure, and current from the coil passed through it. A blue-red discharge resulted; the electrodes were rapidly attacked, and a white substance, probably aluminum bromide, deposited on the inside of the tube. A plate exposed for 30 minutes showed a continous spectrum and lines in the visible identical with the continuous hydrogen spectrum described above. Superposed on this continuous background in the ultraviolet were several lines due to aluminum, and a group of bands between 2880 Å. and 2760 Å. This group consisted of nine bands, arranged in three sub-groups of three each; the spacing in each sub-group and between sub-groups was fairly uniform. These bands occurred outside the limits of absorption for hydrogen bromide; the carrier was not identified, but it is not considered probable that it was hydrogen bromide.

Another attempt was made to excite an emission spectrum of HBr, using active nitrogen. The usefulness of this method has been pointed out by Mulliken.[9] Our apparatus was essentially the same as his. The nitrogen was prepared by heating air in the presence of yellow phosphorus for some time, and passing the resulting gas through concd. sulfuric acid, a phosphorus pentoxide tube, and a liquid-air trap. The liquid-air trap was found necessary to eliminate a brilliant blue spectrum, probably due to phosphorus, which occasionally appeared in the afterglow tube. The spectrum of active nitrogen then appeared in the afterglow tube. On admitting hydrogen bromide to the afterglow tube, the glow disappeared, and a spectrogram showed that the active nitrogen bands had been suppressed completely, or nearly so, in the region of 3300 Å. to 2000 Å., and in the visible region. The only other effects observed on admitting hydrogen bromide were the appearance of a pair of lines at about 3360 Å., and of a system of four bands at about 4000–3650 Å. Since neither of these lies within the limits of absorption for hydrogen bromide, they are not of interest in connection with its absorption spectrum.

Experiments on the Electrical Conductivity of the Illuminated Gas

As ionization is a possible result of the absorption of radiation, efforts were made to test the electrical conductivity of the illuminated gas. Unfortunately the apparatus available was not sufficiently sensitive to give

[9] Mulliken (a) *Phys. Rev.*, **25**, 119, (b) 259 (1924); (c) **26**, 1 (1925).

conclusive results. The conductivity cell consisted of quartz tube No. 1, down one arm of which were inserted parallel tungsten wire electrodes, about 2 mm. apart, sealed through glass which was sealed directly to the quartz with the aid of a graded seal. The tube was filled with hydrogen bromide gas with precautions as to baking out the tube and purifying the gas. Ultraviolet radiation from a cadmium spark source was focused on the region between the two electrodes, and the electrodes were connected to an electroscope. The rate of leak of the charge of the electroscope was observed with and without irradiation. No conductivity was detected; but the high rate of leakage of the cell itself (due to the fact that the electrodes were sealed through the glass only about 0.5 cm. apart) made it doubtful whether currents of the expected order of magnitude could be detected.

Discussion

This investigation has shown within the limits of the accuracy of the spectrograph used that the ultraviolet absorption spectra of hydrogen bromide and hydrogen iodide are continuous, showing no evidence of band structure. This result may be discussed from two points of view: first, that of the theory of molecular band spectra; and second, that of the mechanism of the photochemical decomposition.

The type of molecular absorption spectrum which has hitherto received most attention consists of a system of bands, and is ascribed to excitation of a molecule which, in its initial and final states, is the same chemical species. The separation of the individual lines in the partial bands is greatest for those molecules having the smallest moments of inertia. Hence, a heavy molecule with a large moment of inertia gives an absorption spectrum which might appear continuous, if the dispersion of the spectrograph were not sufficiently great. In the case of hydrogen bromide and iodide, the theory of band spectra indicates that the separation of the partial bands (expressed in wave numbers) should be approximately equal to the wave number of the zero line of the fundamental vibrational-rotational absorption band in the infra-red region of the spectrum. In the section on experimental results, it has been shown that our spectrograph is capable of resolving bands of this separation, but no bands were found.

Since the spectra appear to be continuous, it is logical to attempt to correlate them with the continuous absorption spectra shown by atoms. The absorption of light is continuous for the principal line series spectra of atoms if the frequency of the radiation is greater than the series limit, which corresponds to the complete ejection of an electron from the atom.[10] In other words, the atom becomes ionized, and the final state of the reaction is not merely an excited atom, but a positive ion and an electron. X-ray absorption spectra are another example of this phenomenon. In

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[10] For discussion and references, see article by Harrison, *Phys. Rev.*, **24**, 466 (1924).

the case of the hydrogen halides, it has been shown by Warburg[2] and others that the absorption of ultraviolet light is accompanied by decomposition into hydrogen and halogen. It is difficult to escape the conclusion that in this case, as in cases of truly continuous absorption, the final state of the absorbing molecule is not the same chemical species as the initial state. Possible final states are (1) hydrogen and halogen atoms, (2) hydrogen halide ion and electron, (3) hydrogen ion and halogen ion. Although sufficient evidence is not at hand to make absolutely sure, it seems most probable that the first of these hypotheses is correct, since in determinations of ionization potentials by electron impact in these gases,[11] no ionization is found until the kinetic energy of the electrons is far greater than the energy of the radiation which produces photochemical decomposition. Our preliminary search for a photo-electric effect in hydrogen bromide gas gave a negative result. Moreover, the energy of the absorbed radiation is greater than that necessary for the decomposition of the gases into atoms. These heats of dissociation for the hydrogen halides are given in Table III, along with the absorption limit and the energy[12] corresponding to this wave length.

Table III

Comparison of Photochemical and Thermochemical Energy of Dissociation of Hydrogen Halides

Halide	Absorption limit, Å.	Energy of radiation, cal.	$-\Delta H$ (Thermal decompn.), cal.
HCl	2200	130,000	99,500
HBr	2640	108,000	78,300
HI	3320	86,000	68,000

It has been pointed out by Stern and Volmer[3] that the absorption of energy sufficient to dissociate the molecule is not always accompanied by dissociation. For example, the iodine molecule has absorption bands and gives resonance band spectra in the ultraviolet at wave lengths much shorter than that corresponding to the heat of dissociation. The molecules of hydrogen bromide and iodide, however, do not appear to have absorption bands[13] of this type in the ultraviolet but appear to have

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[11] Compton and Mohler, "Critical Potentials," *Bull. Nat. Research Council,* 9, No. 48 (1924).

[12] This is given by $Nh\nu$, where N is Avogadro's number, h is Planck's constant, and ν is the frequency.

[13] Bands of unusual types have been mentioned by Mulliken [*Phys. Rev.*, 25, 509 (1925)]. The visible absorption bands of iodine gradually merge and "become lost in a region of apparently continuous absorption which probably means that actual dissociation of the molecule is reached or at least closely approached." Also the emission band of calcium hydride, CaH_2, shows a peculiarity which might be attributed to the instability of the molecule in higher vibrational or rotational excited initial states. In addition Mulliken observes the non-occurrence of band emission spectra for polar compounds of the sodium chloride or silver chloride type. Very recently Barker and Duffendack [*Phys. Rev.*, **26**, 339 (1925)] have looked for emission bands in hydrogen chloride in the region 6000 to 2000 Å. in low-voltage arcs and found none.

continuous absorption, which may account for the absence of emission bands.

As regards the mechanism of the photochemical decomposition, two hypotheses have been advanced. Stern and Volmer[3] postulate that the absorption of light produced an electronically excited molecule as the first step, and that in the second step a collision between the excited molecule and a normal molecule resulted in the formation of a hydrogen molecule and a halogen molecule. In view of the previous discussion, this mechanism must be ruled out, since it was shown that the existence of an electronically excited hydrogen halide molecule is highly improbable.

STERN AND VOLMER MECHANISM

(1) HX + radiant energy = HX (excited). (2) HX (excited) + HX (normal) = $H_2 + X_2$.

Warburg's mechanism assumes that the ultraviolet light decomposes a molecule of hydrogen halide into atoms, and that the hydrogen atom on collision with a normal molecule produces a hydrogen molecule and an atom of halogen. The two halogen atoms then unite to form a molecule. This mechanism is shown in the first three of the equations below.

WARBURG'S MECHANISM

(1) HX + radiant energy = $H + X$.

(2) $HX + H = H_2 + X$.

(3) $X + X = X_2$.

(4) $HX + X = X_2 + H$.

(5) $H + H = H_2$.

Equations 4 and 5 represent two other possible secondary reactions. Warburg ruled out Equation 4 on the ground that it is accompanied by an increase in free energy, and so could not take place spontaneously; and he pointed out that Equation 5 has a very small probability of occurrence compared with Equation 2, as the concentration of hydrogen atoms is very small. This mechanism explains the fact, brought out by Warburg's experiments, that one quantum of radiant energy decomposes two molecules of hydrogen halide. The data in Table III show that the energy of the light absorbed is sufficient to bring about Reaction 1, and Warburg showed that Reactions 2 and 3 would be spontaneous. It has been pointed out above that the nature of the absorption spectra indicates such a mechanism, at least as regards the primary reaction. Although Warburg put forward his mechanism before the theory of band spectra had received its great development, no facts have been discovered which disagree with it. Nevertheless, the evidence for it is only circumstantial, and definite proof must await the development of methods of detecting small amounts of hydrogen and halogen atoms, whose duration of existence is probably very short.

Two other possible mechanisms suggested themselves, but were found not to be consistent with the experimental results. The first of these assumed the presence in the gases of polymerized molecules, such as are known to exist in hydrogen fluoride. The absorption spectra of such molecules would possibly appear continuous. Absorption by a double molecule could conceivably produce directly a molecule each of hydrogen and halogen, thus accounting in a simple way for the decomposition of two molecules of HX by one quantum of radiation. If this were the case, however, it would be expected that the absorption would be a function of the temperature and the pressure, since increasing the temperature and decreasing the pressure would both tend to bring about the dissociation of the double molecules. No effect of temperature or of pressure on the absorption was observed by Coehn and Stuckardt, by Warburg, or by ourselves. Photographs of the absorption at 25°, 250° and 400°, on the same plate, keeping the length and conditions of exposure the same (Plates No. 38 and 39, Table I, Nos. 9, 10 and 11) showed no appreciable difference in the nature, limit and intensity of the absorption. Coehn and Stuckardt obtained similar results, and Warburg found the absorption coefficient for the wave lengths he used constant with varying pressure. This mechanism was, therefore, dismissed as improbable. The second possibility was that hydrogen halide molecules are adsorbed on the surface of the quartz vessel, and that this adsorbed film is responsible for the absorption of light and the resultant photochemical decomposition. An adsorbed film, however, would be affected by changes of temperature and pressure in much the same way as polymerized molecules. The above remarks in regard to absorption coefficient also rule out this possibility.

Our conclusions regarding the mechanism of the reaction are as follows. The experiments described, with the aid of the quantum theory of spectra, support the postulate that this is a case of dissociation of a molecule into atoms by the direct action of ultraviolet light. The facts that the absorption spectra are apparently continuous, that two molecules of halide are decomposed per quantum of radiation absorbed, and that the energy of the absorbed radiation is sufficient to produce decomposition of the hydrogen halide molecule into neutral atoms, are strong circumstantial evidence in favor of Warburg's original mechanism for the photochemical decomposition of the hydrogen halides.

Summary

1. Ultraviolet absorption spectra of carefully purified gaseous hydrogen bromide and hydrogen iodide have been photographed at various temperatures and pressures, using a continuous spectrum from a hydrogen discharge tube as a source of radiation.

2. Attempts were made to excite an emission spectrum of hydrogen bromide in the ultraviolet, with an electric discharge through the gas, and with active nitrogen. No emission spectrum which could be attributed to hydrogen bromide was found.

3. An unsuccessful attempt was made to detect photo-electric conductivity in hydrogen bromide gas while illuminated by ultraviolet light.

4. The photographs of the spectra show no band structure,[14] but do exhibit continuous absorption extending from the limit of the quartz region in the ultraviolet to a long-wave limit (absorption limit). This limit has been found to be 2640 Å. for hydrogen bromide and 3320 Å. for hydrogen iodide. The data support the hypothesis that a case of molecular absorption has been found in which the function of the radiation is not to produce a band spectrum, but to produce direct photochemical dissociation of the molecule into atoms.

5. Mechanisms for the photochemical decomposition of the hydrogen halides have been discussed. The mechanism of Warburg is consistent with all the evidence.

CAMBRIDGE A, MASSACHUSETTS

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 96]

THE ADSORPTION OF GASES BY PLATINUM BLACK

BY ARTHUR F. BENTON

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If adsorbed films of gases on solids are in general unimolecular, and if the forces involved are typical valence forces acting between individual molecules in the gas and individual atoms in the solid, then the possibility exists, as Langmuir[1] has pointed out, that the volumes of different gases adsorbed by a given surface may be related stoichiometrically. Thus, each atom in the solid surface might be capable of adsorbing one molecule of certain gases, two molecules of certain others, etc.; in still other cases, two or more atoms of the adsorbent might be equivalent to each molecule of gas. It is evident, however, that these stoichiometric relations could occur only if every atom in the surface of the adsorbent takes part in the process, or at least if the same fraction of the surface is active toward different gases. Pease[2] has shown that this condition is not fulfilled in the case of adsorptions on metallic copper, and Taylor[3] concludes that the same is probably true of contact catalysts in general. Nevertheless, when the forces are particularly powerful, as in the adsorption of numerous gases by platinum,

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[14] Since this manuscript has been written, the absorption spectra of hydrogen bromide at different pressures have been photographed with a spectrograph of much greater dispersion. The photographs show no band structure and the spectra appear continuous. These additional data lend still more support to the assumption that the absorption spectra of the hydrogen halides are truly continuous.

[1] Langmuir, THIS JOURNAL, **40,** 1361 (1918).

[2] Pease, *ibid.,* **45,** 2296 (1923).

[3] Taylor, *Proc. Roy Soc.* (London), **108A,** 105 (1925).

one might anticipate a more uniform covering of the surface, and hence the possibility of adsorptions of different gases in stoichiometric ratios.

Langmuir's experiments[1] on the adsorption of gases at low pressures by a plane surface of platinum foil showed that the maximum volumes of carbon monoxide, oxygen and hydrogen adsorbed were roughly equal, and corresponded with the amount to be expected in a unimolecular layer. The main purpose of the present research was to find whether platinum in the form of platinum black also adsorbs approximately equal volumes of different gases.

This investigation was carried out during my appointment as National Research Fellow in chemistry, and was aided on the financial side by a grant to Professor A. A. Noyes from the Carnegie Institution of Washington.

Previous Work

The adsorption of gases by platinum black has been the subject of numerous investigations.[4] Most of the early work, however, is concerned with only a single gas, usually hydrogen, and as a rule the experimental technique employed was unsatisfactory. The first investigation which is not open to this criticism is that of Mond, Ramsay and Shields.[5] These authors found that similar samples of platinum black adsorbed, at room temperature, approximately equal volumes of hydrogen, oxygen, carbon monoxide and sulfur dioxide. In the method used, however, only one adsorption measurement could be made with a given sample of platinum black, and duplicate determinations with different samples often failed to check satisfactorily.

In an extended study of the adsorption of gases by contact catalysts, Taylor and Burns[6] included measurements on platinum black. The latter was first treated with hydrogen to remove the film of oxygen and then heated in vacuum to 110°, at which temperature it was hoped the hydrogen could be completely removed. However, the experiments reported in the present paper show that more than half of the hydrogen adsorbed by platinum black at room temperature is retained in a vacuum at 110°. It is therefore evident that, owing to reaction with, or displacement of, this large amount of hydrogen in subsequent experiments with other gases, the data obtained by these investigators do not represent the true adsorptions on platinum black. Taylor and Burns did show, however, that carbon monoxide could not be recovered by evacuation.

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[4] For a list of references up to the year 1900, see Bose, *Z. physik. Chem.*, **34**, 710 (1900).

[5] Mond, Ramsay and Shields, (*a*) *Phil. Trans.*, **186A**, 657 (1895); (*b*) **190A**, 129 (1897). These papers may also be found in *Z. physik. Chem.*, **19**, 25 (1896) and **25**, 657 (1898), respectively.

[6] Taylor and Burns, THIS JOURNAL, **43**, 1273 (1921).

Pollard[7] has attempted to measure the adsorption of hydrogen and carbon monoxide by platinized asbestos, but the results appear rather doubtful. He claims to have been able to pump off these gases completely at 0°, if sufficient time was allowed. This result is at variance with all other work in this field, and it seems probable that part of the gas apparently recovered from the platinum was in reality air which had leaked into the apparatus through the stopcocks lubricated with phosphorus pentoxide.

Boswell and McLaughlin[8] have recently published a paper dealing with the adsorption of hydrogen and oxygen by platinum black, in which some extraordinary results are reported. However, a careful consideration of the experimental part of their paper, together with Boswell's previous work[9] on nickel, suggests very strongly that their results were vitiated by the escape of hydrogen from their apparatus through the numerous rubber connections.

Experimental Part

Method.—A survey of previous work in this field shows that it is impossible to free platinum black completely from adsorbed gases without heating it to temperatures at which the black is converted into sponge. Mond, Ramsay and Shields[5] overcame this difficulty to some extent by using a new sample of platinum black for each experiment. In the investigation here reported, on the other hand, the same sample of platinum was used throughout. Care was exercised, however, to avoid the errors of much recent work on this subject, and it is believed that correct measurements of the relative adsorptions of different gases by the same sample of platinum black have been obtained for the first time.

An outline of the method, which is somewhat similar to that employed by Langmuir in his studies[1] on platinum foil, is as follows. The bulb containing the platinum black was exhausted, filled with hydrogen to remove the oxygen previously adsorbed, and then again exhausted for a long time at 110°, in order to complete as far as possible the sintering process which occurs under these conditions. The remaining hydrogen was then removed by treatment with an excess of oxygen and exhaustion to remove the water thus formed. After this treatment oxygen is left on the platinum, and this was eliminated by introducing an excess of carbon monoxide. The bulb was then again evacuated at 110°, and the amount of carbon dioxide formed determined by analysis of the recovered gases. Half this volume of carbon dioxide represents the volume of oxygen previously present. Also, by subtracting the volume of carbon dioxide formed from the volume of carbon monoxide disappearing, the amount of

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[7] Pollard, *J. Phys. Chem.*, **27**, 356 (1923).

[8] Boswell and McLaughlin, *Trans. Roy. Soc. Can.*, [3] **17**, Sec. III, 1 (1923).

[9] Boswell, *ibid.*, [3] **16**, Sec. III, 1 (1922).

carbon monoxide remaining in vacuum at 110° may be calculated. On again introducing carbon monoxide, the total adsorption of this gas under any given conditions could be readily obtained. An analogous procedure was used in determining the adsorptions of oxygen and hydrogen. Thus, for example, the volume of oxygen required to react with the known amount of carbon monoxide remaining in vacuum at 110°, subtracted from the total volume of oxygen disappearing, gave the volume of oxygen retained by the platinum.

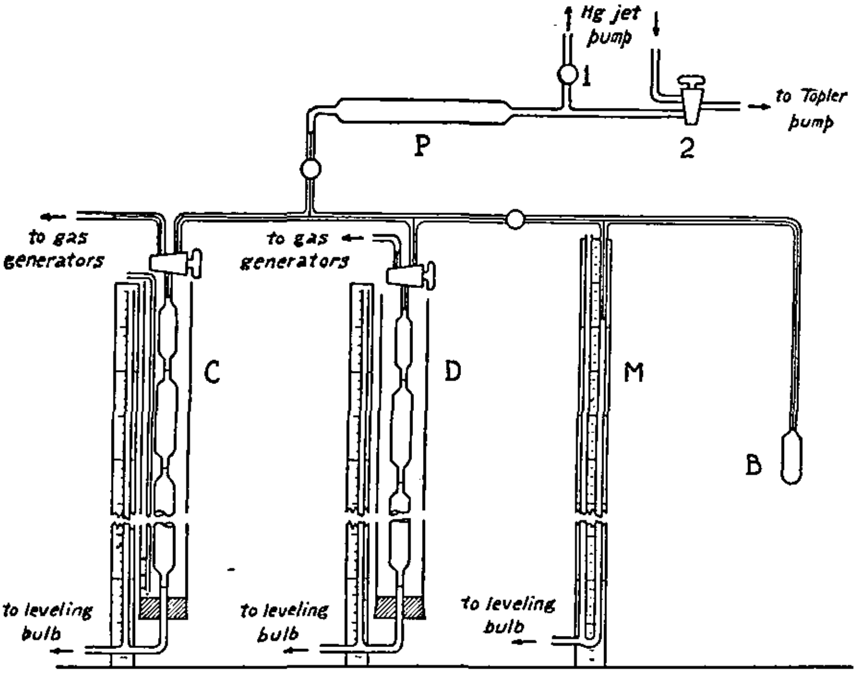

Fig. 1.—Diagram of apparatus.

Apparatus.—The apparatus (Fig. 1) consisted essentially of a bulb (B), containing the platinum black, a constant-volume manometer (M), two gas burets (C,D) connected with the gas generating and purifying lines, a Töpler pump and a mercury-vapor pump. The Töpler pump was so arranged that it could be operated either alone or as fore vacuum for the vapor pump. It was provided with a third gas buret (not shown) for measuring the gases collected, and this in turn communicated with gas analysis apparatus of a modified Orsat type. The pumps were protected from water vapor by the *phosphorus pentoxide* tube P. Gas volumes were determined in the calibrated burets by bringing the mercury level to the most convenient mark, and measuring the pressure exerted by the gas. Fused glass joints were used throughout. The stopcocks marked 1 and 2 were greased with the usual rubber stopcock grease. All others were lubricated with white vaseline which had been heated for some time in a vacuum at 120°. As a lubricant this material proved unsatisfactory on continued use, but it was considered desirable to avoid contamination of the platinum as far as possible.

Materials.—The platinum used in this investigation was freed as far as practicable from all impurities, including iridium. After various unsuccessful attempts with other methods, the separation of the latter metal was effected by repeated fractional precipitation of ammonium chloroplatinate, followed each time by ignition and fractional solution in aqua regia. This cycle of operations was repeated four times.

The platinum black was prepared by slowly adding hot 6% chloroplatinic acid solution, neutralized with sodium carbonate, to an equal volume of boiling 5% sodium formate solution. The precipitate was washed by decantation with hot water until no further test could be obtained for chloride ion. In the first four or five washings a small amount of platinum was removed, due to the fact that it failed to settle within a reasonable time. The product was finally dried on a water-bath and transferred to a bulb, which was sealed to the apparatus as shown in Fig. 1. In this condition the sample weighed 4.316 g. By analogy with similar material prepared by Mond, Ramsay and Shields, it was estimated to contain 0.5% of water and 0.6% of oxygen, and therefore 4.269 g. of platinum.

The gases used in this work were prepared as follows. Hydrogen and oxygen were generated by electrolysis of sodium hydroxide solution between Chromel electrodes, and were purified by successive passage over soda lime, hot copper (copper oxide in case of oxygen) and phosphorus pentoxide. Carbon monoxide was obtained by dropping formic acid on warm, concd. sulfuric acid, and passing the gas over soda lime and phosphorus pentoxide. Carbon dioxide was generated by the action of sulfuric acid on sodium carbonate solution, and purified by conducting it through separate tubes of calcium chloride and phosphorus pentoxide. Helium from a tank was freed from impurities by passage over hot copper oxide, and through active charcoal cooled with liquid air. No rubber connections were used on any of the gas-purifying lines, except rubber stoppers on the generating flasks, and adequate displacement of air before collecting gas was always provided.

Procedure.—Before starting a run the bulb containing the platinum was exhausted at 110° (boiling toluene) until the amount of gas obtained at this temperature in five minutes did not exceed 20 cu. mm. The bulb was then cooled and immersed in a bath at 25°. Evacuation was continued for some time in order to make certain that no leak existed. The line to the pumps was then closed and the gas to be tested was admitted to the bulb from C or D, up to approximately atmospheric pressure. The volume of gas so admitted was accurately measured, and the time of admission was noted. Manometer readings were then made at frequent intervals, usually for a period of 30–50 minutes. The possibility of leak was then again tested for by operating the Töpler pump. The bulb and connecting tubing were next exhausted, at 25° until a good vacuum was obtained, and finally at 110°. The gases pumped off were collected and measured, and analyzed when necessary for carbon dioxide and other gases.

Experimental Results.—The data obtained are summarized in Table I, where the experiments are listed in the order in which they were made. The several columns give (1) the run number, (2) the gas used, (3) the volume admitted to the bulb, (4) the total volume pumped off, (5) the volume of carbon dioxide pumped off (when analysis was made), (6) the volume of gas remaining adsorbed on the platinum in vacuum at 110°, (7) the equilibrium pressure (in mm. of mercury at 0°), (8) the volume of gas in the free space at this pressure, and (9) the volume of gas adsorbed

TABLE I

ADSORPTION DATA

Weight of Pt = 4.269 g.

Run	Gas used	Volume in, cc.	Volume out, cc.	CO_2 out, cc.	Volume remaining at 110°, cc	Pressure (extrapolated), mm.	Volume in free space, cc.	Volume adsorbed at 25°, cc.
3	O_2	16.39	9.30	. .	3.95	688	8.96	4.38
4	H_2	25.14	12.96	...	4.28	743.6	9.69	7.55–7.85
5	H_2	13.09	13.16	...	4.21	755.3	9.84	7.53
6	H_2	12.92	12.97	...	4.16	737.7	9.61	7.52
7	O_2	16.62	9.83	...	4.71	728	9.48	4.96
8	H_2	26.72	13.23	...	4.07	774.3	10.09	7.21–7.51
9	H_2	13.27	13.32	...	4.02[a]	768.0	10.00	7.34
10	CO	15.88	12.19	...	6.21[b]	776	10.11	?
11	O_2	12.53	11.58	6.21	3.34	769.2	10.02	3.39
12	CO	18.12	11.38	6.68	6.74 6.51	766.6	9.98	?
13	CO	11.13	11.17	<0.1	6.70 6.47	770.5	10.04	7.72
14	CO	11.27	11.25	0.00	6.72 6.49	783.9	10.21	7.65
15	O_2	11.49	10.92	6.49	3.81	733.8	9.55	3.88
16	He	9.85	9.89	...	...	756.7	9.85	...
17	O_2	10.04	9.86	0.00	3.99	746.0	9.72	4.13
18	H_2	24.97	12.87	...	4.12	765.4	9.97	7.02–7.32
19	CO_2	13.46	10.61	10.59	(2.85)[b]	781.7	10.18	(3.28)[b]
20	CO_2	10.56	10.34	...	(3.07)[b]	754.4	9.83	(3.58)[b]
21	CO	14.06	11.12	0.0	6.33[b]	766.8	9.99	?
22	O_2	...	...	6.33	...	...	...	...

[a] Between Runs 9 and 10 a slight leak (air) removed 0.08 cc. of hydrogen.

[b] These values are exclusive of the volumes of hydrogen also present. The latter were: in Run 10, 1.42 cc.; in Runs 19 and 20, 4.12 cc.; in Run 21, 0.83 cc.

at 25° and the equilibrium pressure. All volumes are expressed in cc. at 0° and 760 mm. The methods of obtaining the values in Cols. 6–9 are explained below.

A consideration of Runs 12, 11, 10, 9 and 8 will illustrate the method of calculating the values in Col. 6. Thus in Run 12, of the 18.12 cc. of carbon monoxide introduced, 11.38 cc. was recovered, partly as carbon monoxide and partly as carbon dioxide formed by interaction of the monoxide with oxygen remaining from Run 11. The difference, or 6.74 cc., represents the volume of the monoxide which remained adsorbed on the platinum in vacuum at 110° at the conclusion of this run. (The value, 6.51 cc., also given for this run in Col. 6, was obtained by calculating back from the results of Runs 15, 14 and 13.) Furthermore, since 6.68 cc. of carbon dioxide were obtained in Run 12, the volume of oxygen remaining in vacuum at the end of Run 11 must have been half of this value, or 3.34 cc. In Run 11, 6.21 cc. of carbon dioxide was formed and, therefore, this quantity of carbon monoxide must have remained from Run 10. The amount of oxygen recovered as such in Run 11 was 11.58–6.21, or 5.37 cc. Hence the loss of oxygen was 12.53–5.37, or 7.16 cc. But 3.34 cc. was left on the platinum and 3.11 cc. reacted to form carbon dioxide. Therefore, 7.16–3.34–3.11, or 0.71 cc., reacted with hydrogen which had remained from Run 9, incompletely displaced by carbon monoxide in Run 10. Hence at the end of this run the platinum retained 1.42 cc. of hydrogen and 6.21 cc. of carbon monoxide. Accordingly, of the 15.88 cc. of the monoxide introduced in this run, 6.21 cc. was not recovered. The 12.19 cc. of gas pumped off must have consisted, therefore, of 15.88–6.21, or 9.67 cc., of carbon monoxide and 2.52 cc. of hydrogen. Consequently the hydrogen present at the start of Run 10 amounted to 2.52 plus 1.42, or 3.94 cc. Since 0.08 cc. of hydrogen was accidentally removed by a slight leak before this run, the volume of hydrogen remaining at the conclusion of Run 9 was 4.02 cc., as given in Col. 6. In Run 9, 0.05 cc. of hydrogen was pumped off in excess of the amount introduced, and therefore 4.07 cc. of hydrogen must have remained in vacuum at 110° at the end of Run 8. It will be unnecessary to illustrate for the other runs the relatively simple calculations needed to obtain the values given in Col. 6.

To obtain the equilibrium pressures tabulated in Col. 7, Table I, the pressures in the bulb, obtained from the manometer readings, were plotted against the reciprocals of the corresponding times, and the curves extrapolated to infinite time. Some typical curves are shown in Fig. 2. The volumes of gas in the free space of the bulb at these extrapolated equilibrium pressures were then calculated (Col. 8, Table I), making use of the helium experiment (Run 16) on the assumption that this gas was not appreciably adsorbed. In those cases where the same gas was used as in the previous run, the volumes adsorbed at 25° and the equilibrium pressure (Col. 9) were obtained by adding to the volume remaining from the previous run (Col. 6) the volume taken up in the run in question, that is, the difference between Cols. 3 and 8. Thus, for example, in Run 13, 11.13–10.04, or 1.09 cc. of gas was taken up; since 6.63 cc. (average of two values given in Col. 6) was already present as a result of Run 12, the total adsorption in Run 13, at 25° and the equilibrium pressure, was 7.72 cc.

When the gas being tested was different from that used in the previous run, the volume adsorbed at the equilibrium pressure could not ordinarily be calculated, since in these cases the free space was filled with a mixture of two gases. Thus, in Runs 10 and 21 carbon monoxide and hydrogen, and in Run 12 carbon monoxide and dioxide, were present in the free space in undetermined proportions. Similar, but much less uncertainty exists in Runs 4, 8 and 18, where the mixture consisted of hydrogen and water vapor. The two values given in these cases for the adsorption at 25° (Col. 9, Table I) were calculated on the assumption that the free space was free from water vapor, and saturated at 25°, respectively.

The mean of these two is probably not far from the true value. This difficulty may be avoided in Runs 3 and 7, since it was found that the volume of oxygen pumped off was the same, within experimental error, as the volume required to fill the free space at the last measured pressure. Hence, no adsorbed oxygen could be removed by exhaustion at 110° and, therefore, the values given in Col. 6 for Runs 3, 7, 11 and 15 represent also the amounts of oxygen actually adsorbed at 25° and the last measured pressure. The adsorptions at 25° and the equilibrium pressure (Col. 9) were obtained by adding to these values the small additional quantities which would have been taken up on standing indefinitely. For example, in Run 7 the last measured pressure was 746.6 mm., and by extrapolation (Curve 7, Fig. 2) the equilibrium pressure was estimated as 728 mm. This decrease of 18.6 mm. corresponds to a further adsorption of 0.25 cc., and consequently the total adsorption at equilibrium would have been 4.71 + 0.25, or 4.96 cc. It may be noted that Runs 3 and 7 were unique in the slowness with which equilibrium was approached.

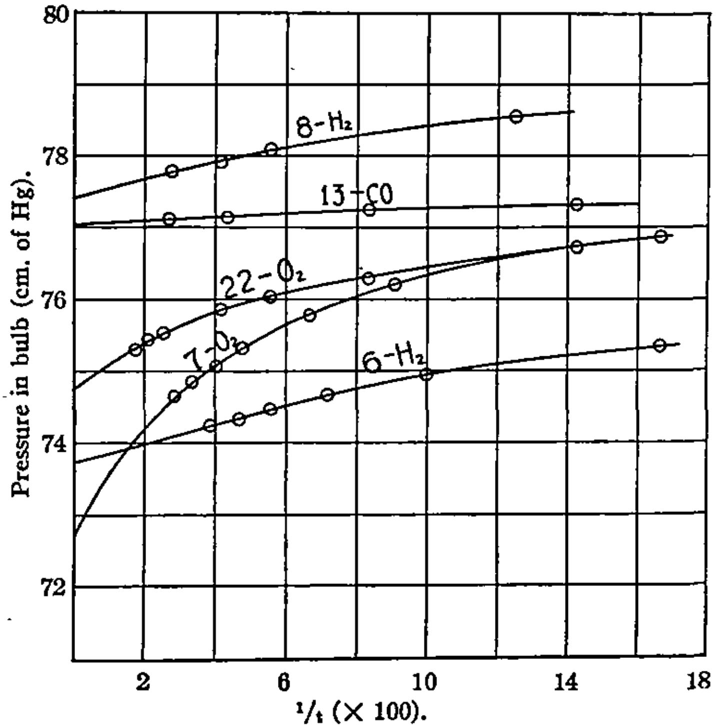

Fig. 2.—Rate of approach to equilibrium. (The curves are numbered to correspond to the run numbers in Table 1.)

Parentheses have been placed around the carbon dioxide adsorptions in Runs 19 and 20 to indicate that these values are doubtless affected by the hydrogen also present (Table I, Note *b*). In fact it seems not improbable that the carbon dioxide and hydrogen interacted to form a very stable surface complex, since it is difficult to account otherwise for the fact that in Runs 19 and 20, only 0.07 and 0.06 cc., respectively, of carbon dioxide were given off in vacuum after the temperature had been raised to 110°.

For the sake of completeness it should be mentioned that the first run with this sample of platinum (Run 1) was made with oxygen, and Run 2 with hydrogen. The results are omitted from Table I because the recovered volumes were not determined. From the volume introduced in Run 2 it was found that the amount of hydrogen adsorbed plus the amount equivalent to the oxygen remaining from Run 1, equaled 45.17 cc. The corresponding value for similar runs made later was, on the average, 15.7 cc., indicating the great sintering effect produced when platinum black is heated to 110° in hydrogen for the first time.

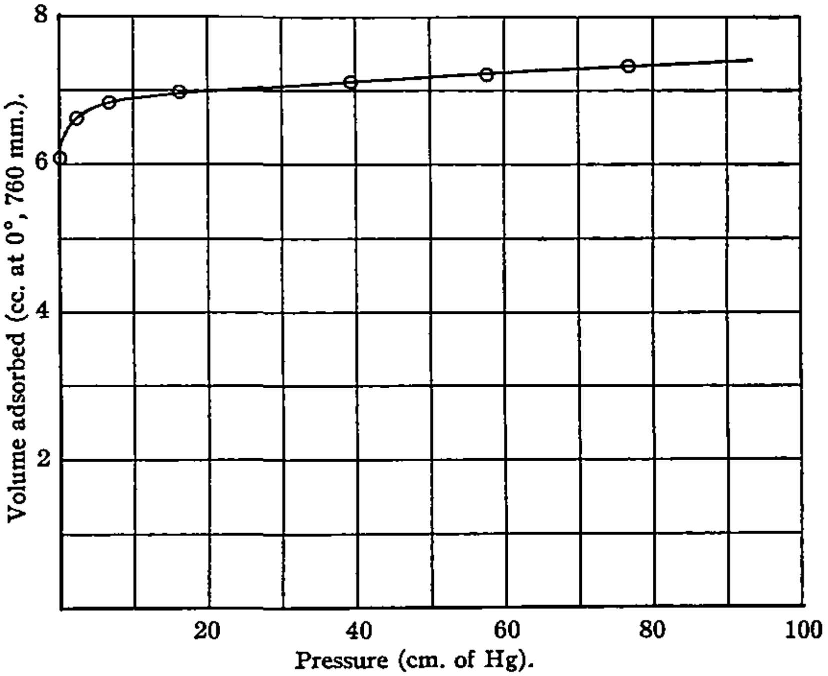

Fig. 3.—25° isotherm for hydrogen.

Isotherms.—In Run 9 the hydrogen was withdrawn in stages, in order to secure data for the 25° adsorption isotherm for this gas. The results are given in Table II, and plotted in Fig. 3.

Complete isotherms were not determined for the other gases, but their general trend may be estimated for carbon monoxide and oxygen. Thus in Runs 13 and 14 the adsorption of the monoxide at approximately atmospheric pressure was 7.72 and 7.65 cc., respectively; the volumes not recovered by evacuation at 25° were 7.20 and 7.22 cc. Though not strictly equilibrium values, the latter could probably have been reduced

TABLE II

ISOTHERM FOR HYDROGEN AT 25°

Pressure (extrapolated), mm.	Total volume in bulb, cc.	Volume in free space, cc.	Volume adsorbed, cc.
768	17.34	10.00	7.34
577	14.73	7.52	7.21
393	12.27	5.15	7.12
162.4	9.10	2.13	6.97
67.8	7.71	0 88	6.83
23.5	6.94	.31	6 63
1.1	6.07	.01	6.06

but slightly by continued pumping, since only about 0.6 cc. more was removed by exhaustion at 110°. Hence, it is evident that the isotherm for carbon monoxide is even flatter than that for hydrogen. The adsorption of oxygen appears to be completely irreversible, since none was removed by evacuation either at 25° or at 110°.

Discussion

Considering the nature of the experiments, the checks obtained in different runs with hydrogen or with carbon monoxide are regarded as satisfactory. A general tendency may, however, be noted for the adsorption to decrease slightly in successive runs, probably owing to a gradual sintering of the platinum.

In Table III are given the average volumes of the different gases adsorbed by unit volume of platinum, assuming the density of the latter to be 21.0. It will be observed that at 25° and one atmosphere, hydrogen and carbon monoxide are adsorbed to practically the same extent, while the adsorption of oxygen is somewhat more than half as great.

TABLE III

AVERAGE ADSORPTION PER UNIT VOLUME OF PLATINUM

Gas	H_2	CO	O_2
At 25° and 1 atm. (approx.)	36.7	37.8	20.4

The question arises as to the effect of temperature and pressure changes on these adsorptions; for evidently a surface can not be regarded as completely covered with a unimolecular gas film, under given conditions, if a small change in temperature or increase in pressure materially increases the adsorption. Conversely, failure of moderate pressure and temperature changes to alter the volume of gas adsorbed would furnish strong evidence in support of the one-layer hypothesis. From a consideration of the isotherms previously discussed, it is plain that the adsorptions of all these gases are affected but little by moderate changes in pressure. The effect of temperature, however, requires further comment.

Numerous investigators have studied adsorptions, especially of hydrogen, by platinum black at different temperatures, but for the most part without concordant results. Nearly all these experiments are unsatisfactory for the present purpose because the samples of platinum used at the lower temperatures had not previously been heated so hot as those employed at higher temperatures, and hence it was to be expected that the latter would have a smaller adsorption capacity.[10] The results of Taylor and Burns[6] are not open to this criticism, and it should be noted that the objection to their work with platinum black previously discussed, namely, the initial presence of hydrogen on the surface, applies equally to the measurements at different temperatures. Therefore, the fact that these authors found almost identical hydrogen adsorptions at 25° and 110° shows that the total adsorption of this gas on a bare surface is likewise nearly independent of temperature in this range. Such data as exist for carbon monoxide indicate that the adsorption of this gas is also affected but little, if at all, by a temperature change from 25° to 110°. As for oxygen, Mond, Ramsay and Shields[5] found the adsorption increased with temperature and Langmuir[1] has made a similar observation for this gas on platinum foil.

These considerations lead to the conclusion that if the experiments recorded in this paper were repeated at somewhat higher temperatures, the carbon monoxide and hydrogen adsorptions would remain unchanged, but the oxygen value would increase. It is perhaps questionable whether the oxygen adsorption would finally become equal to the values for carbon monoxide and hydrogen, but the results for the two latter gases are clearly in harmony with the view that they form on platinum black "saturated" unimolecular layers.

If this view is correct, the surface area of a given quantity of the platinum black may be roughly calculated. The molar volume is approximately 9.30 and, therefore, the volume occupied by each platinum atom is 1.53×10^{-23} cc., and the area assignable to each atom in a platinum surface is 6.2×10^{-16} sq. cm. There are then 1.6×10^{15} atoms per sq. cm., and if the assumption be made that each platinum atom on the surface holds one *atom* of adsorbed gas, there must be 0.80×10^{15} molecules of hydrogen or carbon monoxide adsorbed per sq. cm. of surface. In other words, 3.0×10^{-5} cc. of gas is required to form one sq. cm. of such an adsorbed layer. Since in the present experiments an average of 37.3 cc. was needed per cc. of platinum, it appears that the sample used had a surface area of 1.3×10^{6} sq. cm. per cc., or 6.0 sq. m. per gram.

Summary

The adsorption of hydrogen, carbon monoxide and oxygen by platinum black has been measured at 25° and one atmosphere pressure, and the

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[10] This applies, for example, to the isobars of Mond, Ramsay and Shields (Ref. 5), and to those of Gutbier and Maisch [*Ber.*, 52B, 1368 (1919)].

25° isotherm for hydrogen has been determined. The method employed is believed to be free from the serious errors of other work in this field.

It was found that hydrogen and carbon monoxide were adsorbed to practically the same extent, while the oxygen adsorption was only about half as great. A consideration of the effect of temperature on these adsorptions leads to the conclusion that at somewhat higher temperatures all three gases would be adsorbed in more nearly equal amounts.

Of especial interest is the fact that the results support the hypothesis of unimolecular (or monatomic) adsorbed films.

UNIVERSITY, VIRGINIA

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 97]

THE INTER-IONIC ATTRACTION THEORY OF IONIZED SOLUTES

VI. THE IONIZATION AND IONIZATION CONSTANTS OF MODERATELY IONIZED ACIDS

BY MILES S. SHERRILL AND ARTHUR A. NOYES

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Principles of the Method

The theory of inter-ionic attraction developed by Milner and by Debye and Hückel[1] has been tested and found to account satisfactorily, at any rate at low concentration, for the anomalous behavior of salts, acids and bases which may be assumed to be completely ionized. In case of slightly ionized acids or bases, the effect of ion attraction is small on account of the low ion concentration in such solutions. In the case of acids or bases which lie between these two extremes (the so-called half-electrolytes) the effect is large; and it is the purpose of this paper to apply certain principles derived from the theory to the evaluation from conductance data of the true ionization and of the ion activity of such substances.

The usual method of calculating the ionization of acids from the conductance ratio Λ/Λ_0 becomes inexact in case of moderately ionized acids, since according to the inter-ionic attraction theory the mobility of the ions decreases when their concentration increases. The exact mathematical treatment of this effect has been developed by Debye and Hückel, and they have derived an expression for the ratio of the mobility of a given ion in a solution of (small) ionic strength[2] to the mobility of that ion at zero

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[1] (a) Milner, *Phil. Mag.*, **23**, 551 (1912). (b) **25**, 742 (1913). (c) Debye and Hückel, *Physik. Z.*, **24**, 185, 334, 305 (1923). See also (d) Noyes, THIS JOURNAL, **46**, 1080, 1098 (1924); and (e) Hückel, "Zur Theorie der Elektrolyte," *Ergebnisse der exakten Naturwissenschaften*, Julius Springer, Berlin, 1924, vol. 3, pp. 256–275.

[2] The term ionic strength is here used, as defined by Lewis and Randall [THIS JOURNAL, **43**, 1141 (1921)], to denote one-half of the sum, taken for all the kinds of ions in the solution, of the products of the molal concentration c of each ion by the square of its valence, z, that is, to be equal to $\frac{1}{2}\Sigma(cz^2)$.

concentration, which shows that the fractional decrease in mobility of a given ion at any definite temperature is a function of the ionic strength of the solution. This is the principle that is employed in this article. The exact Debye-Hückel expression, to be sure, is valid only for very small ionic strengths. Moreover, the specific nature of the other ions present in the solution theoretically has an effect even at very small concentrations. Nevertheless, it is to be anticipated that these deviations from the principle will not produce an important effect on the correction on the mobilities, up to moderate concentrations, since the whole correction will be shown to be relatively small, especially when compared with the correction on the ion activities.

On the experimental side, MacInnes[3] has shown, by combining conductance with transference data and assuming complete ionization, that the mobility of certain monatomic univalent ions (H^+, K^+, Cl^-) up to 0.1 N is independent of the other ion with which it is associated, provided the latter is also monatomic and univalent. He mentions, without citing data, that this principle is not accurate when applied to nitrates or chlorates. We have made a similar comparative study of ions in solution of unibivalent salts and uni-univalent salts; this shows that the mobilities of a definite ion (for example, K^+) at a given ionic strength differ considerably from each other in solutions of salts (such as KCl and K_2SO_4) of the two valence types. Nevertheless, this principle gives results sufficiently exact for the purpose, especially if the mobilities used are derived from the known conductances of ions that have the same valence and similar molecular complexity as those existing in the solutions to be investigated.

The method here used of applying this ionic-strength principle for evaluating the mobilities of ions and the ionization of moderately ionized acids from conductance measurements is most readily explained by considering the case of a solution containing a single di-ionic acid H^+A^- at concentration c normal. The equivalent conductance Λ of the acid is determined by its ionization γ and by the ion mobilities u_H and u_A, or by the corresponding ion-conductances Λ_H and Λ_A,

$$\Lambda = \gamma\ (u_H F + u_A F) = \gamma\ (\Lambda_H + \Lambda_A)$$

The value of the sum of the ion conductances at a given ionic strength, which in this case is equal to γc, is obtained by the additivity principle from the equivalent conductances of the completely ionized substances H^+Cl^-, Na^+A^- and Na^+Cl^- at that ionic strength.

This method evidently differs from the usual method of evaluating the ionization of an acid by the relation $\gamma = \Lambda/\Lambda_0$ only in the respect that there is substituted for the Λ_0 value a value corrected for the decreased mobilities of the ions. The applications imply also the assumption that the largely

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[3] MacInnes, This Journal, 43, 1221, 1223 (1921).

ionized substances HCl, NaCl and NaA are completely ionized up to the moderate ionic strengths involved—an assumption which has been made probable by the recent discussions of the theory.

In calculating the ionization constant of the acid by the mass-action expression the so-determined ion concentrations γc must be corrected for the activation which results from the ion attraction, even at smaller ion concentrations. The expression for the ionization constant K then becomes

$$K = \frac{(\alpha_H \gamma c)\ (\alpha_A \gamma c)}{(1-\gamma)c} = \frac{\alpha_H \alpha_A \gamma^2 c}{1-\gamma} \tag{1}$$

Here α_H and α_A represent the activity coefficients or activations of the two ions at the prevailing ionic strength γc.

The ion-attraction theory requires for very small ionic strengths that the activation α_A of any ion A of valence z_A be given by the following equation,[4] when the ion concentrations are expressed in moles per liter.

$$\log_{10} \alpha_A = -1.283 \times 10^{-6} \frac{z^2_A \sqrt{\Sigma(cz^2)}}{(\kappa T)^{1.5}} \tag{2}$$

At higher ionic strengths the size of the ion and nature of the other ions present enter as factors.

This principle, combined with the assumption that at moderate ionic strengths the activations of potassium ion and chloride ion are equal, makes it possible to calculate the separate activation of any ion from the ion-activation products experimentally determined for various salts and acids. This hypothesis was proposed by MacInnes,[5] and employed by Lewis and Randall,[6] in evaluating the activations of the separate ions.

The activations α_H and α_{SO_4} of hydrogen ion and of sulfate ion at various ionic strengths were obtained by applying these principles to the ion-activation products for potassium chloride and hydrochloric acid recently derived by Scatchard[7] and to those for potassium sulfate derived by us from the freezing-point measurements of Hall and Harkins[8] and of Hovorka and Rodebush[9] by the methods[10] of Lewis and Randall and of Scatchard.

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[4] See Noyes, Ref. 1d, p. 1095.

[5] MacInnes, *ibid.*, **41**, 1088 (1919).

[6] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., **1923**, p. 381.

[7] Scatchard, THIS JOURNAL, **47**, 644, 654 (1925).

[8] Hall and Harkins, *ibid.*, **38**, 2674 (1916).

[9] Hovorka and Rodebush, *ibid.*, **47**, 1619 (1925). Rodebush, *ibid.*, **48**, 709 (1926). Our computed values of $(\alpha_K^2\ \alpha_{SO_4})^{\frac{1}{3}}$ agree completely with those recently published by Rodebush, which furnish a striking confirmation of the validity of the limiting form of the Debye-Hückel equation for unibivalent salts.

[10] Values of the quantity j as defined in terms of freezing-point lowering by Lewis and Randall [Ref. 6, Equation 2, p. 342] were obtained by the procedure employed by Scatchard, assuming it to have, in accordance with the Debye-Hückel theory, for a unibivalent salt at 0°, the form $j = 1.30\ c^{\frac{1}{2}} - \beta c$. Here β is a constant for a given salt, which we derived for potassium sulfate (as equal to 2.77) from the value of j correspond-

These activation values are given in Table I. They refer partly to 0° and partly to 25°; but the small change with the temperature is here disregarded.

TABLE I

ACTIVATION OF HYDROGEN AND SULFATE IONS AT VARIOUS IONIC STRENGTHS

Ionic strength	*0.001*	*0.005*	*0.010*	*0.020*	*0.050*	*0.100*	*0.200*
$(\alpha_K\alpha_{Cl})^{\frac{1}{2}} = \alpha_K = \alpha_{Cl}$	0.966	0.927	0.900	0.867	0.813	0.767	0.717
$(\alpha_H\alpha_{Cl})^{\frac{1}{2}}$	.966	.931	.909	.880	.836	.802	.778
$(\alpha_K{}^2\alpha_{SO_4})^{\frac{1}{3}}$	.934	.860	.814	.755	.661	.583	...
α_H	.966	.935	.918	.893	.860	.839	.844
α_{SO_4}	.872	.741	.665	.573	.437	.336	...

For convenience in finding the activations of these ions at other ionic strengths, values of the logarithms of these ion activations were plotted against the square root of the ionic strength.

For finding the activation of the other anions ($H_2PO_4^-$, HSO_3^-, HSO_4^-) of the acids involved in this investigation, values of the ion-activation products are lacking. Therefore, Equation 2, representing the ion-attraction theory at very small ionic strengths, was employed for this purpose in the following form which it assumes for univalent ions in water solutions at 25°.

$$\log_{10} \alpha = -0.357\sqrt{\Sigma(cz^2)} \tag{3}$$

It is doubtless true that the activation values thus obtained are somewhat in error; but, in view of the fact that the anions of most oxygenated acids (such as NO_3^-) do not deviate greatly from the theory, the error is probably not very large.

Ionization Relations of the First Hydrogen of Phosphoric Acid

The best conductance data available for the calculation of the sum of the equivalent conductance at 18° of H^+ and $H_2PO_4^-$ at different ionic strengths are brought together in Table II.

TABLE II

MOLAL CONDUCTANCES OF THE IONS OF PHOSPHORIC ACID AT 18°

Concn. c	NaH_2PO_4	HCl	NaCl	$H^+ + H_2PO_4^-$
0.000	70.0	378.3	108.99	339.3
.001	66.22	375.9	106.49	335.6
.005	65.21	372.6	103.78	334.0
.010	63.86	369.3	101.95	331.2
.020	60.28	365.5	99.62	326.2
.050	57.55	358.4	95.71	320.2
.100	53.95	351.4	92.02	313.3

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ing to the actual freezing-point lowering (0.05005°) at 0.01 molal. Values of the activation product $(\alpha_K^2\ \alpha_{SO_4})^{\frac{1}{3}}$ or mean activation up to 0.01 molal were obtained by substituting this expression for j in the general relation between mean activation and molality given by Lewis and Randall (as Equation 3 on p. 343 of Ref. 6). For concentrations above 0.01 molal the mean activations given for potassium sulfate by these authors (in the table on p. 362 of their "Thermodynamics") were changed in the proportion which their value at 0.01 molal bears to our value at 0.01 molal.

The concentrations c in the first column (expressed as formula weights per liter) represent also the ionic strengths, since all of the ions are univalent. The values for the molal conductance of sodium dihydrogen phosphate are those given by Abbott and Bray,[11] as corrected by them for the slight increase in conductance due to the secondary ionization of the $H_2PO_4^-$. Those given for hydrochloric acid and sodium chloride were determined by Goodwin and Haskell,[12] and by Kohlrausch and Maltby,[13] respectively. The values recorded in the last column were obtained by subtracting at each concentration (or ionic strength) the molal conductance of the sodium chloride from the sum of the other two molal conductances.

Table III contains in the second column the observed values of the molal conductance of phosphoric acid (H_3PO_4) at the concentrations c (in formula-weights per liter) at which they were actually measured by Noyes and Eastman.[14] The third column gives the ratios of these values to the extrapolated value 339.3 for zero concentration. The values of λ therefore represent the ionization calculated under the old assumption of constant ion mobilities. The fourth column shows the values ($\Lambda_H + \Lambda_A$) of the sum of the conductances of the H^+ and $H_2PO_4^-$ ions at the ionic strengths (which for this purpose may be taken equal to λc) prevailing in the phosphoric acid solutions. These values were obtained by graphical interpolation from a plot of the data given in the last column of Table II against the cube root of the concentration. In the fifth column are given the ratios which represent the ionization γ calculated by the principle that the ion mobilities are determined solely by the ionic strength. The next two columns contain the activations α_H and α_A of the ions H^+ and $H_2PO_4^-$ derived as described above. The next to the last column contains the values of the ionization constant calculated in the old way under the assumption that the ions have the same mobility and the same activation (unity)

TABLE III

IONIZATION AND IONIZATION CONSTANT OF PHOSPHORIC ACID AT 18°

Concn. c	Λ for H_3PO_4	$\lambda = \Lambda/\Lambda_0$	$\Lambda_H + \Lambda_A$	$\gamma = \Lambda/(\Lambda_H+\Lambda_A)$	α_H	α_A	$\frac{\lambda^2 c}{1-\lambda}$	$\frac{\alpha_H \alpha_A \gamma^2 c}{1-\gamma}$
0.0000	339.3	1.000	339.3	1.000	1.000	1.000	...	...
.0020	283.1	0.834	335.7	0.843	0.958	0.954	0.0084	0.0083
.0125	191.2	.563	332.2	.575	.927	.908	.0091	.0082
.0500	122.7	.362	327.2	.375	.896	.853	.0103	.0086
.1000	96.5	.285	324.1	.298	.879	.818	.0113	.0091

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[11] Abbott and Bray, THIS JOURNAL, 31, 748 (1909).

[12] Goodwin and Haskell, *Phys. Rev.*, 19, 369 (1904).

[13] Kohlrausch and Maltby, Landolt-Börnstein-Roth-Scheel "Physikalisch-chemische Tabellen," Julius Springer, Berlin, 1923, vol. 2, p. 1079.

[14] Noyes and Eastman, *Z. physik. Chem.*, 70, 353 (1910). No correction was applied for secondary ionization of the acid, since the value of the ionization constant for the second hydrogen shows it to be negligible.

at all concentrations. The last column shows the ionization constant obtained by correcting in the way above described for the change in ionization and in activation with the ionic strength (which is equal to the product γc).

It will be seen from Table III that the corrected ionization γ is larger than the conductance ratio Λ/Λ_0 by 2.1% at 0.0125 *F* and by 4.4% at 0.10 *F*. These differences are not large; but upon the value of the ionization constant they would have a much greater percentage effect. The correction for the activation is much larger than that for the mobility; thus the product $\alpha_H\alpha_A$ has the value 0.842 at 0.0125 *F* and the value 0.719 at 0.100 *F*. It will be seen that the effect on the ionization constant of the two corrections combined is small at the smallest concentration 0.0020 *F*, but becomes large at 0.10 *F*, with the result that the corrected values of the ionization constant shows much less variation with the concentration. Indeed, the corrected values are substantially constant between 0.0020 and 0.0500 *F*, though the ionization of the acid changes from 84.3 to 37.5%. The values show, to be sure, a definite trend at the higher concentrations. This may be due to the fact that the actual activation α_A of $H_2PO_4^-$ (like that of IO_3^-, for example) becomes less than the assumed value calculated by equation (2), which is strictly valid only for very small ionic strengths, or to the fact that the assumption used in calculating α_H is somewhat in error.

The results show that the true ionization constant of the first hydrogen of phosphoric acid has the value of 0.0083 at 18°.

Ionization Relations of the First Hydrogen of Sulfurous Acid

The conductance of sodium hydrosulfite has been measured by Barth,[15] Jellinek,[16] and Lindner.[17] Of these measurements the most careful seem to be those of Lindner; and though they refer to only two concentrations, they have been used here for determining the values of $\Lambda_H + \Lambda_{HSO_3}$. The results are given in Table IV. The values given for hydrochloric acid and sodium chloride were interpolated from the data of Bray and Hunt.[18]

TABLE IV

MOLAL CONDUCTANCES OF THE IONS OF SULFUROUS ACID AT 25°

Concn.	$NaHSO_3$	HCl	NaCl	$H^+ + HSO_3^-$
0.00	100.3	422.2	125.8	396.7
.00437	96.1	415.8	121.1	390.8
.03760	90.4	401.4	112.9	378.9

That the values are not seriously affected by the secondary ionization of HSO_3^- into H^+ and $SO_3^=$ is shown by the fact that the increase between

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[15] Barth, *Z. physik. Chem.*, **9**, 181 (1892).

[16] Jellinek, *ibid.*, **76**, 340 (1911).

[17] Lindner, *Monatsh.*, **33**, 613 (1912).

[18] Bray and Hunt, THIS JOURNAL, **33**, 786 (1911).

0.0376 and 0.00437 *F* is 6.3% for sodium hydrogen sulfite, while it is 7.3% for sodium chloride—thus even less for the former salt.[19] The value (100.3) given in the table for sodium hydrogen sulfite at zero concentration was found by increasing the values at each of the two higher concentrations by the same percentage amount as the value for sodium chloride increases between each of these concentrations and zero concentration, and taking the mean of the two results (100.7 and 99.9).

The conductance of sulfurous acid has been measured by Barth,[15] by Kerp and Baur,[20] and by Lindner.[17] The results of the last two investigations are reproduced in the second column of the upper and lower sections of Table V. That table also presents the calculated values of the ionizations, activations and ionization constants in exactly the same way as those for phosphoric acid in Table III. The values of $\Lambda_H + \Lambda_A$ were obtained by plotting the last two values of this quantity given in Table IV against the cube root of the corresponding concentrations, and interpolating on the straight line connecting the two points for the ionic strengths prevailing in the measured sulfurous acid solutions. The other quantities were computed in the same way as before; thus α_A for the HSO_3^- was again obtained by Equation 3 representing the theory at small concentrations.

TABLE V

IONIZATION AND IONIZATION CONSTANT OF SULFUROUS ACID AT 25°

Concn c	Λ for H_2SO_3	$\lambda = \Lambda/\Lambda_0$	$\Lambda_H + \Lambda_A$	$\gamma = \Lambda/(\Lambda_H + \Lambda_A)$	α_H	α_A	$\frac{\lambda^2 c}{1-\lambda}$	$\frac{\alpha_H \alpha_A \gamma^2 c}{1-\gamma}$
0.00	396.7	1.000	396.7	1.000	1 000	1.000	...	...
.00817	267.9	0.675	389 8	0.687	0.933	0.917	0.0115	0.0105
.0536	165.6	.417	382.4	.433	.888	.838	.0160	.0132
.5058	68.4	.172	370.9	.184	.841	.701	.0182	.0124
.01261	244.5	.616	388 3	.630	.924	.902	.0125	.0113
.02498	207.6	.523	385.6	.538	.907	.874	.0143	.0123
.04972	169.5	.427	382.7	.443	.890	.841	.0158	.0131
.1000	134.5	.339	379.4	.354	.872	.803	.0174	.0136
.2583	88.3	.223	375.0	.235	.854	.751	.0165	.0120
.5236	65.3	.164	371.0	176	.841	.703	.0169	.0116

Here again, it is seen that the corrected ionization values γ are not very much greater than the values λ calculated under the assumption of constant mobility, but that the differences are great enough to have a considerable effect on the ionization constant. The activation correction has, as

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[19] The values that were obtained by Jellinek for the ionization constant of hydrosulfite ion by different methods are so discordant as to have little significance. His final average value 5×10^{-6} is much larger than his own conductance data and those of Lindner indicate. Barth's conductances, to be sure, show a larger increase with decreasing concentration, thus of about 15% between the two concentrations in the table; but it seems almost certain that this early work is unreliable.

[20] Kerp and Baur, *Arb. kaiserl. Gesundheitsamt.*, **26**, 297 (1907); *C. A.*, **4**, 264 (1910).

before, a much larger effect upon the constant, and it causes the values of it to show much smaller variations with the concentration.[21]

As the best value at 25° of the true ionization constant, as derived from these conductance data, 0.012 may be adopted. It may be pointed out that, though the data are not very satisfactory, there is a fair agreement between the two series of constants, derived from the data of Lindner and of Kerp and Baur.

Ionization of Hydrosulfate Ion in Solutions of Sulfuric Acid

It seems of special interest to apply the principles derived from the ion-attraction theory to the ionization relations of sulfuric acid, both because it involves a case where both hydrogens of the acid are ionized, and because better knowledge of the ionization constant of the second hydrogen of this important acid is very desirable.

Noyes and Stewart[22] drew certain conclusions as to its ionization relations by combining transference data and conductance data. Their conclusions were, however, based on the assumption that ion mobilities are independent of ion concentration, that the ions have the activities of perfect solutes, and that the ionization of the first hydrogen of sulfuric acid is equal to that of hydrochloric acid as determined by its conductance ratio.

It is now possible to interpret these data much more accurately with the aid of the new principles. It is still necessary, however, to make some assumption as to the ionization of the first hydrogen of the acid; and the simplest and most probable one is to regard it as completely dissociated up to the moderate concentrations involved. It will be seen later that the results afford justification of this hypothesis. Conductance data alone do not make possible a solution of the problem, as was the case with the acids considered above, since exact knowledge of the equivalent conductance of the HSO_4^- ion is not available. By combining transference numbers with the conductances, however, the conductance of this ion can be eliminated or it can be determined.

Consider a solution containing c formula weights of H_2SO_4 per liter, in which the hydrosulfate ion has an ionization γ. There are then in the solution, per formula weight of acid, $(1 + \gamma)$ moles of H^+, $(1-\gamma)$ moles of HSO_4^- and γ moles of $SO_4^{=}$. If Λ_H, Λ_{HSO_4} and $2\Lambda_{SO_4}$ represent the

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[21] Thus while the values of $\lambda^2c/(1-\lambda)$ increase from 0.011 to 0.016 between 0.0082 and 0.0536 molal, according to Lindner's measurements, those of the corrected ionization constant change only from 0.0105 to 0.0132; or in the case of Kerp and Baur's measurements the increase between 0.013 and 0.100 molal of the uncorrected values is from 0.012 to 0.017, while the increase of the corrected values is only from 0.0113 to 0.0136. At the higher concentrations, 0.26 or 0.51 molal, both series show a decrease of the ionization constant, but the effect of new factors, such as viscosity of the solution, doubtless here comes into play.

[22] Noyes and Stewart, This Journal, 32, 1133 (1910).

molal conductances of these ions at the ionic strength prevailing in the solution, the molal conductance 2Λ of the acid will be given by the equation

$$2\Lambda = (1 + \gamma)\,\Lambda_H + (1-\gamma)\,\Lambda_{HSO_4} + \gamma 2\Lambda_{SO_4} \qquad (4)$$

The corresponding expression for the hydrogen transference-number τ_H, which is equal to the equivalents of hydrogen migrating into the cathode portion as H^+ minus the moles of HSO_4^- migrating out of it, is as follows

$$\tau_H = \frac{(1 + \gamma)\,\Lambda_H - (1 - \gamma)\,\Lambda_{HSO_4}}{2\Lambda} \qquad (5)$$

Solving these two equations, we get

$$\gamma = \frac{\Lambda + \Lambda\tau_H - \Lambda_H}{\Lambda_H + \Lambda_{SO_4}} \quad (6); \qquad \text{and} \qquad \Lambda_{HSO_4} = \frac{\Lambda - \Lambda\tau_H - \gamma\,\Lambda_{SO_4}}{1 - \gamma} \qquad (7)$$

In order to solve Equation 6 for the ionization γ of the hydrosulfate ion, values of Λ_H and Λ_{SO_4} at the ionic strength prevailing in the solution must be known. This ionic strength is readily seen to be $c\ (1 + 2\gamma)$. The conductance and transference data available for calculating these ion-conductances at 25° at various ionic strengths are brought together in Table VI. The transference numbers were obtained by graphical interpolation from a plot of the experimental values,[23] or at zero concentration of the values corresponding to the separate ion conductances.[24] The table also contains the values of Λ_{Na} (later required), obtained by subtracting from the equivalent conductance of sodium sulfate the values of Λ_{SO_4}.

TABLE VI

CONDUCTANCES OF HYDROGEN ION, SULFATE ION AND SODIUM ION AT 25°

Formal concn.	Equivalent conductance Λ for HCl^{18}	$K_2SO_4^{25}$	$Na_2SO_4^{25}$	τ_H in HCl	τ_{SO_4} in K_2SO_4	Λ_H in HCl	Λ_{SO_4} in K_2SO_4	Λ_{Na} in Na_2SO_4
0.0	422.2	152.6	129.0	0.822	0.514	347	78.4	50.6
.001	420.4	144.8	122.3	.823	.512	346	74.1	48.2
.002	418.6	....	....	.824	..	...	..	..
.0025	...	139.8	117.5	..	.510	344.7	71.3	46.2
.005	415.3	134.4	112.55	.824	.508	342.2	68.3	44.2
.01	411.6	128.1	106.95	.825	.506	339.6	64.8	42.1
.02	406.7	....	....	.826	..	...	..	..
.025	...	118.15	97.9	..	.504	335.9	59.5	38.4
.05	398.4	109.9	90.1	.826	.506	329.1	55.6	75.1
.10	390.4	101.4	81.6	.827	.507	322.9	51.4	30.25
.20	380.2	....	....	.827	..	314.4	..	..

With the aid of interpolated values of Λ_H and Λ_{SO_4} corresponding to those of Table VI, there can be calculated by Equation 6 the ionization of the hydrosulfate ion in any solution of sulfuric acid for which the equivalent conductance Λ and transference number τ_H have been measured.[26]

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[23] Noyes and Falk, THIS JOURNAL, 33, 1457 (1911).

[24] Noyes and Sherrill, "Chemical Principles," Macmillan Co., N. Y., 1922, p. 120.

[25] Noyes and Falk, THIS JOURNAL, 34, 470 (1912).

[26] The values of Λ_H and Λ_{SO_4} prevailing in any sulfuric acid solution are determined by estimating its ionic strength $c(1 + 2\gamma)$ and interpolating from a graph in which the

Table VII contains these values of the ionization γ and the conductance and transference data (as adopted by Noyes and Stewart[27]) from which they are derived. Values of Λ_{HSO_4} calculated by Equation 7 are also given in the table,[28] as they are to be used later.

TABLE VII

IONIZATION AND CONDUCTANCE OF HYDROSULFATE-ION IN SULFURIC ACID SOLUTIONS AT 25°

Formal concn.	Λ for H_2SO_4	τ_H for H_2SO_4	Λ_H	Λ_{SO_4}	γ	$\frac{1}{2}\Sigma(cz^2)$	Λ_{HSO_4}
0.00	425.4	0.816	347.0	78.4	1.000	0.0	..
.00025	413.7	.816	346.2	76.3	0.959	.0007	..
.001	390.8	.816	344.0	74.3	.874	.0027	..
.005	336.8	.816	338.9	69.5	.668	.0116	46.8
.00625	327.5	.816	337.9	68.6	.632	.0141	46.0
.0125	299.2	.816	334.4	65.6	.522	.0255	43.5
.0250	273.0	.816	330.0	62.3	.423	.0461	41.4
.0500	251.2	.816	324.4	58.8	.344	.0844	39.7

From these values of the ionization the molal concentrations of the H^+, $SO_4^=$ and HSO_4^- are readily calculated; and by multiplying these by the ion activations the activities (a_H, a_{SO_4}, a_{HSO_4}) of these ions are obtained, which when substituted in the mass-action expression give the true ionization constant. Table VIII contains the results of these calculations.

TABLE VIII

IONIZATION CONSTANT OF HYDROSULFATE ION IN SULFURIC ACID SOLUTIONS AT 25°

Formal concn.	γ	10^3c_H	$10^3c_{SO_4}$	$10^3c_{HSO_4}$	α_H	α_{SO_4}	α_{HSO_4}	$\frac{c_H c_{SO_4}}{c_{HSO_4}}$	$\frac{a_H a_{SO_4}}{a_{HSO_4}}$
0.00025	0.959	0.490	0.240	0.010	0.971	0.888	0.969	0.0118	0.0105
.001	.874	1.874	.874	.126	.949	.798	.941	.0130	.0105
.005	.668	8.340	3.340	1.660	.912	.647	.883	.0168	.0112
.00625	.632	10.20	3.950	2.300	.905	.621	.871	.0175	.0113
0125	.522	19.03	6.525	5.975	.885	.537	.830	.0208	.0119
025	.423	35.57	10.57	14.43	.863	.449	.779	.0260	.0130
.050	344	67.20	17.20	32.80	.844	.355	.714	.0352	.0148

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ion conductances given in Table VI are plotted against the cube roots of the ionic strengths. From these values a more exact value of the ionization (and ionic strength) is obtained by Equation 6. The calculation is then repeated with this value of the ionic strength; this method of approximation being repeated till no further change in the value of γ results. It may be mentioned that the so-calculated value of γ is not very sensitive to errors in the transference number T_H; thus, in the worst case (the 0.05 F solution) an error of 1% in T_H, corresponding to one of about 5% in T_{SO_4}, makes an error of 1.5% in γ.

[27] Noyes and Stewart, Ref. 22, pp. 1139, 1140. It is striking that the transference numbers of sulfuric acid do not change with its concentration; but this may be due to compensation between the varying proportion of HSO_4 in the solution and the changing mobilities of the various ions.

[28] The calculated values of Λ_{HSO_4} at the lower concentrations are omitted, since they are very inaccurate, owing to large multiplication of errors.

It will be seen from Table VIII that, while the mass-action expression in terms of ion concentrations, even though in deriving them correction was made for various ion mobilities, increases 3.0 fold between 0.00025 and 0.05 formal, the expression in terms of activities increases only 1.4 fold. The latter variation is, to be sure, by no means insignificant; but when it is considered that the ionization varies from 0.959 to 0.344 and the ionic strength from about 0.0007 to 0.084, and that the ionic-strength principle used in calculating the conductances and activations is doubtless inexact at the higher ionic strengths, a variation of this magnitude might well have been expected.[29]

As the best value of the true ionization constant (in terms of activities) the number **0.0115** may be adopted, as this was found at concentrations (0.005–0.0125 *f*) where the ionization (67–52%) was so great as not to cause large multiplication of errors in the calculations, and where the ionic strength is so small that the ionic-strength principle is still probably fairly exact.

Ionization of Hydrosulfate Ion in Sodium Hydrosulfate Solution

It is possible to calculate the ionization constant of the hydrosulfate ion also from the conductance data for sodium hydrosulfate which were obtained by Stewart.[30] The equivalent conductance Λ of this salt is given in terms of the ionization γ of the hydrosulfate ion and the equivalent conductances of the separate ions at the prevailing ionic strengths by the equation

$$\Lambda = \Lambda_{Na} + (1 - \gamma)\,\Lambda_{HSO_4} + \gamma\,\Lambda_H + 2\gamma\,\Lambda_{SO_4} \qquad (8)$$

This equation is readily solved for the ionization γ. Values for Λ_{Na}, Λ_H and Λ_{SO_4} at various ionic strengths have already been given in Table VI; and from plots of these the required values at intermediate ionic strengths were obtained. To find the needed values of Λ_{HSO_4}, the values

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[29] It may be noted that the mean activity coefficient of sulfuric acid, as defined by Lewis and Randall (Ref. 6, p. 328), in these dilute solutions can be calculated from the data of Table VIII, it being equal to $(\alpha_H{}^2\alpha_{SO_4}(1 + \gamma)^2\gamma/4)^{\frac{1}{3}}$. At the concentration 0.0125 formal, which is favorable for such a calculation, the activity coefficient (0.503) thus found is considerably lower than that (0.584) obtained by interpolation from the values given by Lewis and Randall (Ref. 6, p. 357). The discrepancy is doubtless largely due to the fact that their method of evaluation involved extrapolation of the freezing points of sulfuric acid solutions to zero concentration; for this procedure is inexact in the case of this substance, owing to the presence of HSO_4^- in large and rapidly varying proportions. Our value, though it involved extrapolating the freezing points of potassium sulfate solutions, is to be regarded as the more exact one; and therefore all of the values for the activity coefficient above this concentration tabulated by Lewis and Randall should be corrected by multiplying them by the proportionality factor 503/584 or 0.86. It may also be mentioned that this corresponds to a correction of +265 cal. in the value (—176,500 cal.) given by them for the free energy of formation of $SO_4^=$ at activity 1 molal.

[30] Ref. 22, p. 1156.

given in Table VII were also plotted against the cube root of the corresponding ionic strengths, and the best representative straight line was drawn between the points.

Table IX contains the data and calculated ionization values, displayed in the same form as in Table VII. The ion activations correspond to those given in Table I, or in the case of HSO_4^- ion to those calculated from the theory by Equation 3.

TABLE IX

IONIZATION OF HYDROSULFATE ION IN SODIUM HYDROSULFATE SOLUTIONS AT 25°

Formal concn.	Λ	Λ_H	Λ_{SO_4}	Λ_{Na}	Λ_{HSO_4}	γ	$\frac{1}{2}\Sigma(cz^2)$
0.000391	530.97	345.7	75.7	49.2	49.8	0.966	0.0011
.000781	516.75	344.5	74.6	48.6	49.0	.943	.0022
.001562	494.50	342.7	73.1	47.4	48.0	.905	.0044
.003125	463.30	340.3	70.9	45.9	46.7	.851	.0084
.00625	424.76	337.3	68.0	44.1	45.2	.784	.0160
.0125	381.42	333.0	64.5	41.9	43.3	.707	.0302
.025	337.73	328.2	61.1	39.6	41.1	.628	.0564
.050	297.00	322.0	57.6	36.8	38.3	.556	.1056
.100	261.67	314.3	53.9	33.2	34.8	.500	.2000

A confirmation of the principles involved in this method of calculating the true ionization from conductance data is afforded by a comparison of the value of the transference number of the sulfate constituent in 0.1 formal sodium hydrosulfate solution as experimentally determined by Stewart[31] with that calculated from the data of Table IX by the equation $\Lambda T_{SO_4} = 2\gamma\Lambda_{SO_4} - 2(1-\gamma)\Lambda_{HSO_4}$. These two values of the transference number, 0.346 (measured) and 0.339 (calcd.), are in fair agreement with each other.

Table X contains the values of the ionization constant calculated both from the ion concentrations and from the ion activities (a_H, a_{SO_4}, a_{HSO_4}). The ion activations α_H and α_{SO_4} were interpolated from those given in Table I. The values of α_{HSO_4} were calculated from the ion-attraction theory by Equation 3.

TABLE X

IONIZATION CONSTANT OF HYDROSULFATE ION IN SODIUM HYDROSULFATE SOLUTIONS AT 25°

Formal concn.	γ	$10^3c_{HSO_4}$	10^3c_H or $10^3c_{SO_4}$	α_H	α_{SO_4}	α_{HSO_4}	$\frac{c_H\,c_{SO_4}}{c_{HSO_4}}$	$\frac{a_H\,a_{SO_4}}{a_{HSO_4}}$
0.000391	0.966	0.01335	0.3772	0.965	0.863	0.962	0 0107	0.0092
.000781	.943	.0448	0.7364	.953	.814	.946	.0121	.0099
.001562	.905	.1481	1.414	.939	.754	.926	.0135	.0103
.003125	.851	.4641	2.661	.921	.685	.899	.0153	.0107
.00625	.784	1.350	4.900	.901	.604	.863	.0178	.0112
.0125	.707	3.662	8.840	.878	.512	.817	.0213	.0117
.0250	.628	9.300	15.70	.856	.417	.759	.0265	.0125
.0500	.556	22.20	27.80	.838	.319	.685	.0348	.0136

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[31] Ref. 22, p. 1156.

These results show, as in the case of sulfuric acid, that while the mass-action expression in terms of concentrations increases very greatly between 0.0004 and 0.0500 F (thus 225%), yet in terms of activities it shows only a moderate increase (one of 48%). Here again, for the same reasons as in the case of the sulfuric acid results, the value 0.0115 at the intermediate concentrations is to be regarded as the best value of the ionization constant.

It will be noted that this value is identical with that derived from the measurements with sulfuric acid, even though the various ions are present in very different proportions from those prevailing in the sodium hydrosulfate solution. Since un-ionized H_2SO_4, if it existed in the solutions, would be present in much larger proportion in the sulfuric acid solution, this agreement confirms the assumption that the ionization of the first hydrogen of this acid is substantially complete.

The value 0.0115 is much lower than the values 0.02–0.03, found by previous investigators[32] without taking into account the mobility and activity corrections.

Summary

This article describes a method of calculating more accurate values of the ionization of moderately ionized acids than have been heretofore obtained from the ratio Λ/Λ_0 involving the assumption of constant ion-mobilities. Values of the corresponding ionization constants were then calculated in terms of the activities of the ions, whose activations were determined by the usual methods. The principles employed are that the mobility and the activation of a given kind of ion are determined by the ionic strength of the solution, not being dependent on the nature and concentration of the separate ions which give rise to this ionic strength.

The method was applied to calculating the ionizations and ionization constants of the first hydrogens of phosphoric and sulfurous acids, and of the second hydrogen of sulfuric acid, assuming its first hydrogen to be completely dissociated. The relatively small variations of the resulting ionization constants afford justification of the method employed.

Incidentally, the work has led to more reliable values of the ionization constants of these important acids, expressed in terms of activities; namely, to 0.0083 for H_3PO_4 at 18°; 0.012 for H_2SO_3 at 25°; and 0.0115 for HSO_4 at 25°.

PASADENA, CALIFORNIA

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[32] Noyes and Stewart, Ref. 22, p. 1160. Kolthoff, *Rec. trav. chim.*, **43**, 207 (1924). See also Livingston, THIS JOURNAL, **48**, 52 (1926).

[Contribution from the Chemical Laboratory of Harvard University]

THE TRANSMISSIONS OF THE OLDENBERG CHLORINE FILTER FOR λ 2537

By Donald Statler Villars[1]

Received April 6, 1926 Published July 6, 1926

As λ 2537 of the mercury spectrum is quite active photochemically, it is desirable to have a filter which would transmit this line alone and separate the rest of the ultraviolet radiation which is emitted by a quartz mercury lamp. For this purpose Peskov[2] measured the extinction coefficients of chlorine and bromine by microscopic densitometry and calculated therefrom the optimum concentrations (Br_2, 0.0046 *M*; Cl_2, 0.176 *M*—about 4 atm.) for a monochromatic filter. As bromine[3] absorbs λ 2537 appreciably, Oldenberg[4] used a filter containing pure chlorine at a pressure of 6.5 atmospheres and this absorbs the lines from 2654 to 4078 Å., inclusive. Quantitative information concerning the transmissions of such a filter is desirable and so I have measured the absorptions by the method of photographic photometry.

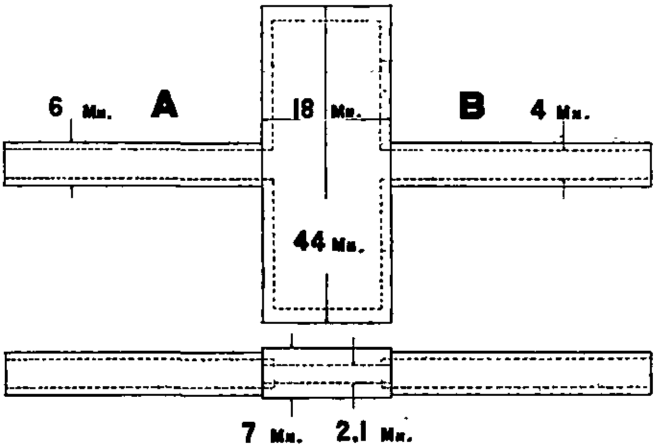

Fig. 1.

The filter was made as follows. Along the edge of a clear Vitreosil plate 44 × 18 × 2.5 mm. was fused a quartz ribbon about 2 mm. thick and to the top of this was sealed another plate of equal size. To appropriate places on opposite edges where some of the ribbon had been omitted, 4mm. quartz tubing was connected (Fig. 1). This quartz work was done by the Macalaster Bicknell Company. The walls of the quartz tubing near the cell were thickened at A and B and the end B was joined to a long tube,

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[1] National Research Fellow in Chemistry.

[2] Peskov, *Z. wiss. Phot.*, **18**, 235 (1919); *J. Russ. Phys.-Chem. Soc.*, **47**, 918 (1915).

[3] Coehn and Stuckardt, *Z. physik. Chem.*, **91**, 722 (1916).

[4] Oldenberg, *Z. Physik*, **29**, 328 (1924).

the other end of which was connected by a DeKhotinsky seal to a small chlorine tank kept at the constant temperature of 15°. To displace the air, chlorine was passed through the cell which was then sealed off at A. The valve was opened and closed, and after being immersed in liquid nitrogen the cell was sealed off at B. Liquid chlorine was present in the completed filter at room temperature, because it had condensed into the cell from the long delivery tube during the sealing operation. The drops disappeared at a temperature of 47.1° (corresponding to a pressure of 13.8 atm.). The cell was heated successfully to 90° without explosion.

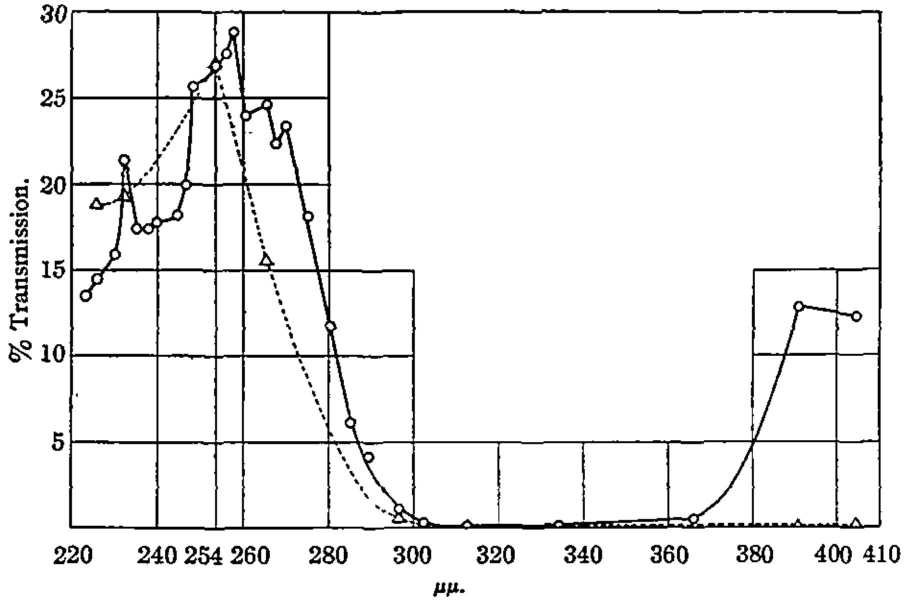

Fig. 2.————— Oldenberg filter. Average depth of Oldenberg filter = 0.21 cm. – – – – Calculated transmissions of a similar Peskov filter. Concn. of Cl_2 = 0.269*M* (19.0°).

The method of photographic photometry used was that developed by Harrison.[5] Nine exposures of equal time intervals were made on the same plate and the intensity I of the light was varied by inserting in the light path oscillating calibrated screens or the chlorine filter. From the D-log I characteristic curve for each wave length and the D (density of the negative) corresponding to the chlorine filter can be calculated $-\log I/I_0 = A$, from the latter the per cent. transmission T. Table I gives values of A and T for wave lengths between 2232 and 5461 Å. In Fig. 2, T is plotted against λ. The dotted curve represents the calculated transmissions of a Peskov filter of such thickness (0.584 cm.) as to give the same transmission of λ 2537 as the Oldenberg filter I used. A comparison of the two curves indicates that the Peskov filter is more nearly monochromatic.

[5] Harrison and Hesthal, *J. Optical Soc. Am.*, **8**, 471 (1924). Harrison, *ibid.*, **10**, 157 (1925); **11**, 113 (1925); *Phys. Rev.*, **24**, 466 (1924).

TABLE I

TRANSMISSIONS OF OLDENBERG AND PESKOV FILTERS

λ	A_1	A_2	A_{Av}	T_0	T_P
2232	0.85	0.89	0 87	13.5	
2259	.81	.86	.84	14.5	18.8
2302	.79	.80	.80	15.9	
2323	.66	.68	.67	21.4	19.24
2352	.75	.77	.76	17.4	
2378	.74	.77	.76	17 4	
2399	.74	.76	.75	17.8	
2447	.74	.74	.74	18.2	
2464	.68	.71	.70	20.0	
2482	.58	.59	.59	25.7	
2537	.57		.57	26.9	27.0
2560	.56	.55	.56	27.6	
2576	.53	.55	.54	28.9	
2603	.62	.62	.62	24.0	
2653	.58	.63	.61	24.6	15.53
2675	.66	.63	.65	22.4	
2699	.62	.64	.63	23.4	
2752	.74	.74	.74	18.2	
2804	.93	.93	.93	11.8	
2853	1.15	1.26	1.21	6.17	
2894	1.36	1.39	1.38	4.17	
2967	1.93	1.96	1 95	1.12	0.52
3024	2.54	2.57	2.56	0.28	0.04
3128	>3.42	>3.42	>3.42	< 0.04	0.00
3341	>2.95	>3.02	>2.99	< 0.10	
3660	2.31	2.28	2.30	0.50	0.01
3907	0.90	0.87	0.89	12.9	
4047	.77	1.04	.91	12.3	0.06
4354					0.89
4938	.56	0.64	.60	25.2	
5461	.43	.42	.43	37.2	

A_1 = —log I/I_0 for exposure No. 1.
T_0 = % transmission of Oldenberg filter.
T_P = calcd. % transmission of Peskov filter.
d = 0.21 cm. = thickness of Oldenberg cell.
C = 0 269 M = concn. of chlorine in cell at temp. at which measurements were made (19.0°).

I wish to acknowledge my indebtedness to Dr. J. B. Green of the Jefferson Physical Laboratory, Harvard University, who checked the values of the wave lengths recorded on the photographs.

Summary

The transmissions of the Oldenberg chlorine (6.45 atm. or 0.269 M) filter are given for wave lengths between 2232 and 5461 Å. and compared with those of a Peskov filter (Cl_2, 0.176 M + Br_2, 0.0046 M). The former filter is more readily made but the latter is more nearly monochromatic.

CAMBRIDGE 38, MASSACHUSETTS

[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS, UNITED STATES DEPARTMENT OF COMMERCE]

THE DISSOCIATION OF POTASSIUM IODIDE AND THE ABSORPTION SPECTRA OF IODINE AND POTASSIUM IODIDE[1]

BY WALLACE R. BRODE

RECEIVED APRIL 17, 1926 PUBLISHED JULY 6, 1926

In papers by Brannigan and Macbeth[2] and by Getman,[3] the absorption spectra of inorganic halides have been discussed and data collected especially on the alkali halides. Getman, who confined his experiments to various chlorides, showed that with an increase in concentration and an equivalent decrease in cell thickness there was an increase in the extinction coefficient of the band; and since it was assumed that the percentage of ionized chlorine in solution increases with dilution, it was stated that this absorption band could not be due to the free halogen ions. Brannigan and Macbeth performed the same experiments with potassium iodide and drew the same conclusions. In addition they pointed out that the band could

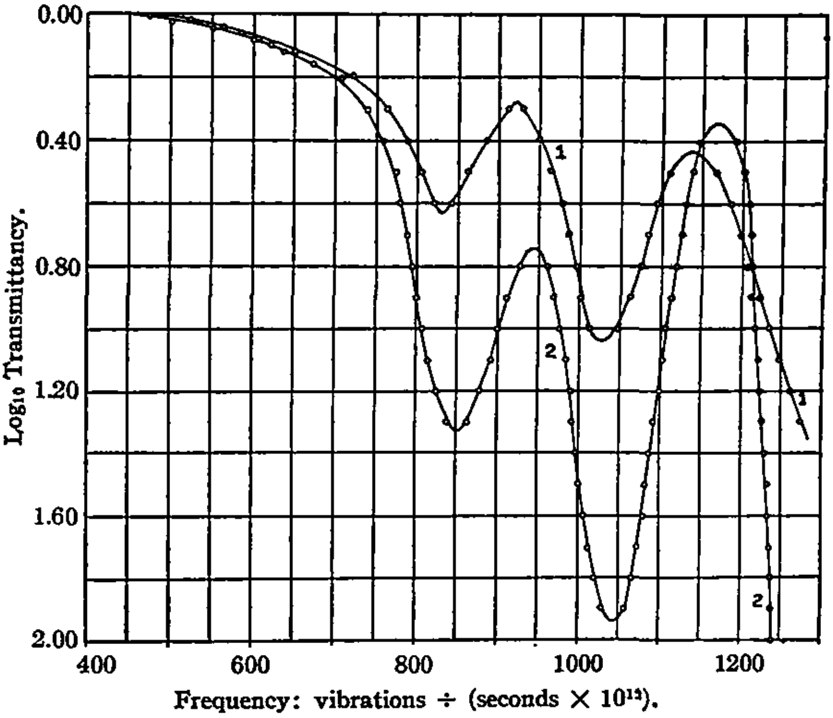

Fig. 1.—The absorption spectrum of iodine in (1) alcohol and (2) potassium iodide solution. Concentration = 0.0003N. Cell thickness = 1 cm. Concentration of KI in potassium iodide solution = 0.125 g. per liter of solution.

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[1] Published by permission of the Director of the National Bureau of Standards of the United States Department of Commerce.

[2] Brannigan and Macbeth, *J. Chem. Soc.*, 109, 1277 (1916).

[3] Getman, *J. Phys. Chem.*, 29, 853 (1925).

not, in the case of chlorine, be due to free halogen as the absorption band of this in the form of a gas was at 918*f*,[4] whereas the observed absorption band in chloride solutions was at 1119 *f*. They did not, however, take into consideration the fact that the absorption band of the halogen in the vapor state might not be the same as in the dissolved state, and in all probability it is not. At least, we do know that iodine does not necessarily give the same colors in a vapor as in the dissolved state and, as shown by the observations made in this work, the first absorption band in the aqueous solution of iodine in potassium iodide is practically the same in frequency as that determined for the small satellite band observed in a very concentrated solution of potassium iodide. Assuming that this satellite band in the concd. potassium iodide solution is due to free iodine, the amount present may be estimated (approximately, of course, as there must be some solu-

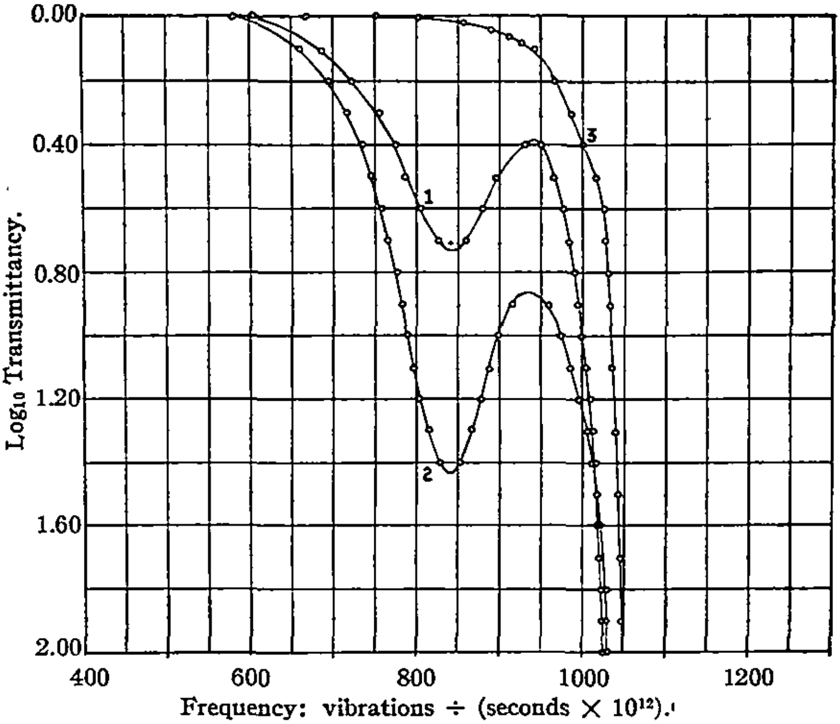

Fig. 2.—(1) The absorption spectrum of a 4 *N* potassium iodide solution; cell thickness = 4 cm. (2) The absorption spectrum of a 4 *N* potassium iodide solution after exposure to north light for three days; cell thickness = 2 cm. (3) The absorption spectrum of a 4 *N* potassium iodide solution after the addition of 8 drops of 0.1 *N* sodium thiosulfate solution to 50 cc. of solution.

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[4] *f* = vibrations ÷ (seconds × 10^{12}). For a description of the method employed see *Sci. Paper*, 440 (1922) of the Bureau of Standards; Brode, *J. Phys. Chem.*, 30 (1926), or Brode and Adams, This Journal, 46, 2033 (1924), Gibson and others, *J. Optical Soc. Am.*, 10, 169 (1925).

tion effects), and it was found to be about 0.000383 g. per 100 g. of potassium iodide, or the equivalent in absorption to a 0.0002 *N* solution of iodine in potassium iodide.

If this band were due to free iodine dissolved in the potassium iodide solution, the addition of a small amount of sodium thiosulfate should completely remove it. Curve 3 of Fig. 2 shows the absorption when a small amount of sodium thiosulfate was added to the potassium iodide solution. The absorption band, so pronounced in Curves 1 and 2, is completely suppressed.

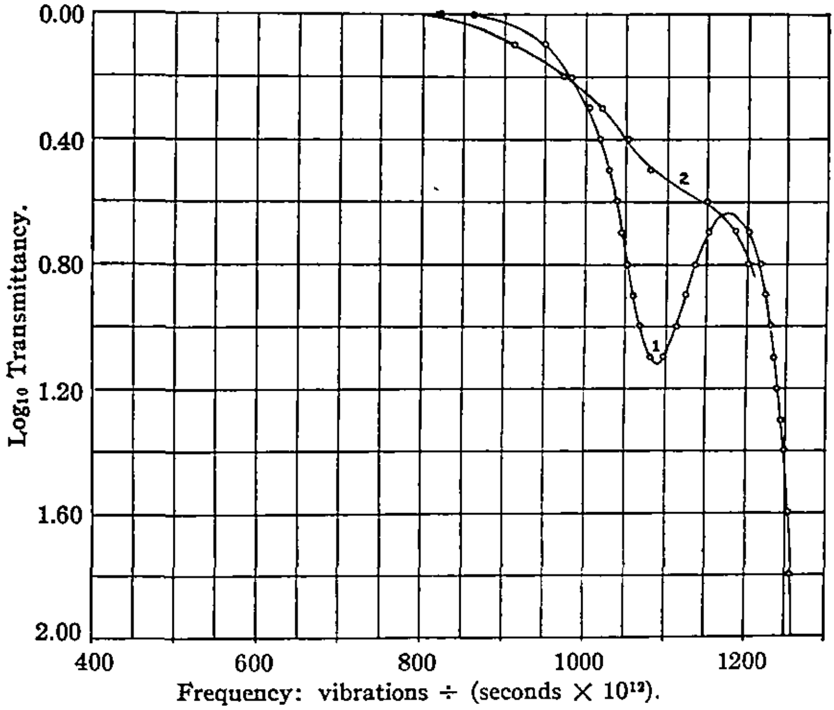

Fig. 3.—(1) The absorption spectrum of a 4 *N* potassium bromide solution; cell thickness = 4 cm. (2) The same solution after the addition of 8 drops of sodium thiosulfate to 50 cc. of solution; cell thickness = 4 cm.

The same experiment was then tried with a potassium bromide solution with similar effect (Fig. 3). These effects were measured by adding exactly the same amount of sodium thiosulfate to both the halide solution and the comparison solvent so as to eliminate as far as possible any absorption due to the sodium thiosulfate. The sodium thiosulfate absorbed further out in the ultraviolet to such an extent as to prohibit the use of the chloride solutions in this series of experiments.

If this band were due to free iodine and the solution which was known to contain a small amount of dissolved oxygen were exposed to light the amount of iodine in solution should increase. Exposure to north light for three days caused an increase in the extinction coefficient from 0.045 to 0.178 corresponding to nearly four times the amount of free iodine found in the original sample. The frequency and shape of this latter curve were the same as those of the unexposed sample, indicating that the band in both cases was due to the same cause. The addition of sodium thiosulfate to this solution containing the intensified band removed it exactly as before.

The fact that the concentrated solutions of potassium iodide fail to follow Beer's law in regard to this satellite band and that the extinction coefficient actually increases with an increase in the concentration of the potassium iodide in solution does not invalidate the suggestion that this band is due to the free halogen. There is little doubt that a reaction of this type which liberates free iodine is promoted by the high concentration of the potassium iodide. With a decrease in the concentration of the potassium iodide one should expect greater stability in the solution and less tendency to liberate free iodine. As indicated by the absorption curves of potassium iodide as compared with that of iodine, there is a strong absorption band characteristic of this salt in the ultraviolet beyond the second iodine band, and it is entirely possible that in the dilute solutions required to observe this band, Beer's law is followed. On the other hand, it is unreasonable to expect solutions of a concentration nearly that of saturation to display dilution effects of a linear order.

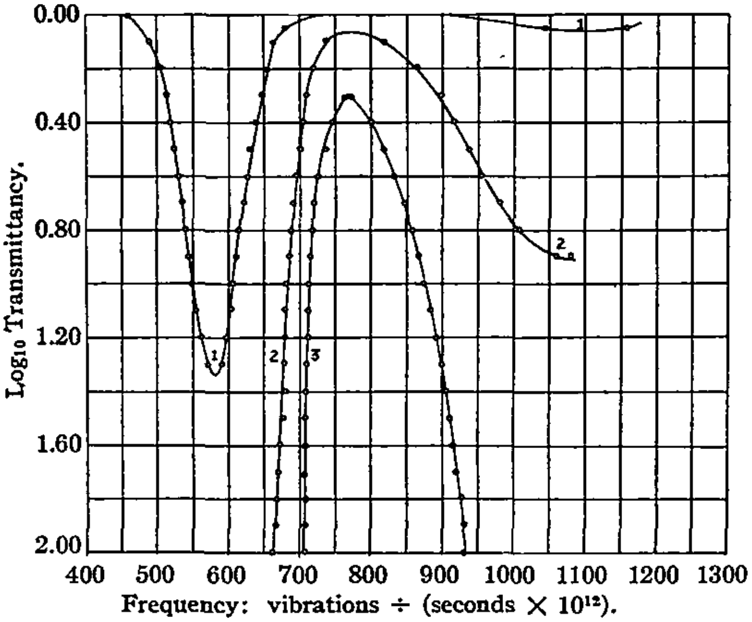

Fig. 4.—The absorption spectrum of iodine in carbon tetrachloride. (1) Concentration = 0.003 *N*; thickness = 1 cm. (2) Concentration = 0.03 *N*; thickness = 1 cm. (3) Concentration = 0.03 *N*; thickness = 4 cm.

The absorption spectrum of iodine in potassium iodide solution exhibits a higher extinction coefficient and a slightly greater frequency than that of iodine in alcohol. The absorption spectrum of iodine in carbon tetrachloride is similar to the spectrum of iodine in the vapor state, whereas the brown color in the case of alcohol and aqueous potassium iodide solutions indicates that there is some solution effect which as yet is not satisfactorily explained. The fact that the absorption spectra curves of iodine in alcoholic and in aqueous potassium iodide solutions are nearly identical in general shape and frequency range would indicate that the condition of iodine in both of these solutions in certain fundamental respects is the same.

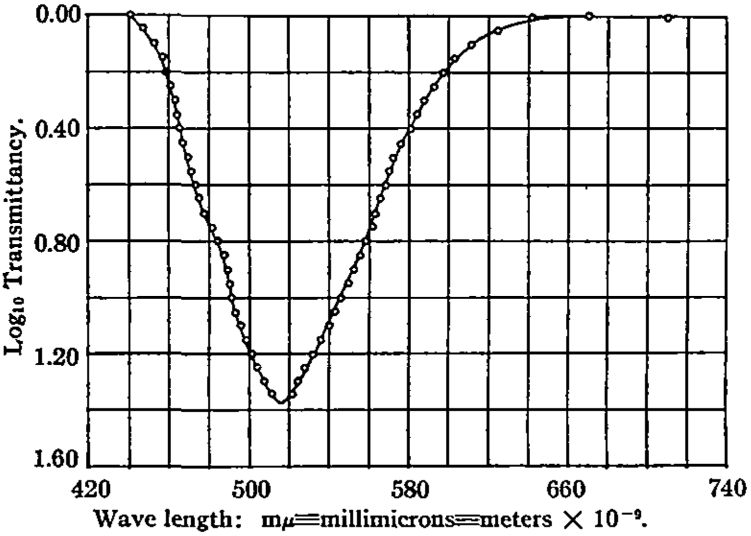

Fig. 5.—The absorption spectrum of iodine in carbon tetrachloride, (visual only). Concentration = 0.0003 *N*; cell thickness = 10 cm.

The absorption spectrum of iodine in carbon tetrachloride is remarkable for its high transmission in the ultraviolet and were it not for the high volatility of the solvent, such a solution might find considerable use as a light filter to exclude visible light. Care must be taken to make sure that the solvent contains no alcohol or similar impurity as the presence of less than 1% of alcohol will give the alcohol band instead of the carbon tetrachloride band.[5] This is an effect analogous to the effect of alcohol on the absorption spectra of benzene-azophenol in carbon tetrachloride and benzene.[6]

Summary

1. The absorption spectra of iodine have been determined in alcohol, aqueous potassium iodide and carbon tetrachloride.

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[5] Lachman, This Journal, 25, 50 (1903). For a complete discussion of the color of iodine solutions see Mellor, "Inorganic and Theoretical Chemistry," Longmans, 1922, vol. II, p. 110.

[6] Brode, *J. Phys. Chem.*, 30, 56 (1926).

2. The absorption spectra of potassium iodide have been examined under various conditions and it has been found that the satellite band has the same frequency of vibration as the first band of iodine in a potassium iodide solution and can be completely removed with sodium thiosulfate.
3. It has been shown that this satellite band is due to the presence of free iodine dissolved in a solution of potassium iodide and not to the potassium iodide.
4. The use of iodine dissolved in carbon tetrachloride as a light filter to remove visible light and transmit most of the ultraviolet light to a frequency of 1150 *f* (the cut-off point of the solvent) has been suggested.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

THE VAPOR PRESSURE OF ANHYDROUS OXALIC ACID

BY W. ALBERT NOYES, JR., AND DELBERT E. WOBBE

RECEIVED APRIL 17, 1926 PUBLISHED JULY 6, 1926

In connection with some work on the thermal decomposition of anhydrous oxalic acid[1] it became necessary to know the vapor pressure of anhydrous oxalic acid at temperatures ranging from 120° to 170°. Since anhydrous oxalic acid decomposes quite rapidly in this temperature range it is obvious that direct measurements of the vapor pressure of the anhydrous solid would be very difficult to carry out at these temperatures and that values obtained would be of doubtful accuracy. It seemed advisable to carry out measurements at lower temperatures and to obtain an equation which could be used for purposes of extrapolation.

Some preliminary measurements were made by a static method. Oxalic acid was recrystallized thrice from water and then placed in a flask of about 500cc. capacity sealed to a vacuum line. The flask was surrounded by a salt solution kept at its boiling point (about 105°) and the flask evacuated to as low a pressure as could be obtained with a mercury diffusion pump backed by an efficient oil pump. The evacuation was carried on for 20 to 30 hours. During this time a large portion of the oxalic acid sublimed and condensed along the outlet tube of the flask. The material remaining was usually quite lumpy. The flask was broken off and the outlet covered over with a rubber tip. The lumps were then broken by tapping. The material was kept in a desiccator over phosphorus pentoxide. The preliminary measurements were made by placing some of the anhydrous material in a spiral tube connected with an ordinary manometer. This system was evacuated to as low a pressure as could be obtained with a mercury diffusion pump and was then placed

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[1] To be published in the near future.

in an air thermostat capable of regulation to about 0.1°. After sufficient time had been allowed to elapse so that temperature equilibrium was attained, the difference in level was read on the manometer and the vessel removed and plunged into cold water as quickly as possible to stop thermal decomposition. The difference in level was read at room temperature. By making the assumption (later found to be justified) that anhydrous oxalic acid has too low a vapor pressure to be read by ordinary means at room temperature, it is possible to calculate what the pressure exerted by the decomposition products would be at the temperature of the thermostat and to subtract this value from the pressure measured. There are several difficulties in this method. In the first place, according to Berthelot and Gaudechon[2] oxalic acid decomposes in two ways at least: (1) directly into carbon dioxide, carbon monoxide and water or into carbon dioxide and hydrogen; (2) into formic acid and water, the formic acid subsequently giving carbon dioxide and hydrogen or carbon monoxide and water. Any water formed would, if its pressure were high enough, form $H_2C_2O_4.2H_2O$ at the lower temperature. The vapor pressure of water over hydrated oxalic acid has been carefully determined by Baxter and his co-workers,[3] so that if the decomposition proceeded entirely by any one method a calculation of the vapor pressure would still have been possible from this type of data. Unfortunately, this did not seem to be the case and in addition adsorption of the products of decomposition by the glass walls and by the oxalic acid seemed to play a very large role. Consequently this method may be said to give only the order of magnitude. The results we obtained when compared to the results later to be given did indicate that oxalic acid vapor was not greatly associated if at all.

A dynamic method was finally adopted. The volumes of several 5-liter bottles were accurately determined (within about 0.02%) by allowing water from a carefully calibrated volumetric flask to drain into them and filling up the small volume at the end from a calibrated buret. For example, four determinations for one of the bottles gave 4954.0, 4954.8, 4954.3, 4954.3. These bottles were fitted with rubber stoppers and stopcocks and were well dried and then filled with nitrogen dried by passage over calcium chloride. The temperature of the nitrogen was determined at the beginning of the run and the nitrogen was displaced by means of glycerol. The nitrogen subsequently passed through calcium chloride and phosphorus pentoxide drying tubes and through a flowmeter which was used to determine roughly the rate of flow. The gas next passed through about 4.5 meters of tubing inside of the thermostat before passing over the anhydrous oxalic acid. The latter was well distributed in a tube

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[2] Berthelot and Gaudechon, *Compt. rend.*, **158**, 1791 (1914).

[3] Baxter and Lansing, THIS JOURNAL, **42**, 419 (1920). Baxter and Cooper, *ibid.*, **46**, 923 (1924).

about 12 mm. in diameter and 75 cm. long. The oxalic acid was placed at least 10 or 12 cm. below the level of the liquid in the thermostat. The gas emerging from the thermostat passed through a tube more than a meter long. Most of the oxalic acid condensed just above the level of the liquid in the thermostat, and it was assumed at the beginning that no error had been introduced by assuming complete condensation in the tube. This assumption was found not to be justified. Accordingly, a U-tube was sealed to the end of the outlet tube and was immersed in an ice-water mixture. After the conclusion of the passage of the gas, the liquid was withdrawn from the thermostat to a point about 12 cm. below its former level, the tube was carefully washed off and then sealed with an oxygen flame at a point sufficiently removed from the condensed oxalic acid to preclude the possibility of any decomposition. The tip of the tube was broken off inside an Erlenmeyer flask and the tube washed out with dil. sulfuric acid. The resulting solution was titrated with approximately 0.01 *N* potassium permanganate solution. This solution was made by dilution from a solution of approximately 0.1 *N* potassium permanganate that had been standardized both by iron wire and by hydrated oxalic acid which had been shown to be about 99.98% pure by titration with sodium hydroxide. A set of weights calibrated by the method described by Richards[4] and using a 2g. weight standardized by the Bureau of Standards as the absolute standard, was used. The values obtained by means of the oxalic acid are as follows: 0.09202, 0.09212, 0.09207, 0.09209, 0.09209, 0.09213; av., 0.09209. The values obtained by the iron wire method are 0.09202, 0.09222, 0.09190; av., 0.09205. The value used was 0.09207, from which the largest deviation was 0.18%.

In titrating, the solution was warmed and a blank was always run, using the same volume of the dil. sulfuric acid. The color intensities were matched in Nessler tubes, and the amount required for the blank was subtracted from the amount used in the titration of the unknown. It was found that the titration was not accurate unless the colors matched were very faint, preferably with not more than one drop of the 0.01*N* permanganate in excess.

There are several important sources of error in the method as used. (1) If the oxalic acid is associated in the vapor state, our values would all be in error. The fact that the logarithm of the pressure when plotted against the reciprocal of the absolute temperature gives a fairly straight line would indicate that the degree of association at least remained constant in the temperature interval studied. We have already mentioned the evidence obtained in the preliminary work. (2) Any decomposition of the oxalic acid in the bath would cause a larger volume of gas to pass out than we had thought and would probably make our results too high. By

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[4] Richards, This Journal, 22, 144 (1900).

extrapolation of our results on thermal decomposition this error was shown to be much less than 0.1% even at the highest temperature used. (3) The volume of gas at the temperature of the thermostat was calculated by means of the formula $v = a(t - t_0)v_0 + v_0$, where v is the volume at the temperature of the thermostat, t is the temperature of the thermostat, t_0 is the temperature of the gas at the beginning of the run, v_0 is the volume of the bottle and $a = 0.003672$.[5] This assumes that the temperature of the drying columns remained constant and that the gas was as dry when its volume was determined as after it had passed through the drying columns. Neither of these assumptions is strictly justified, although any error introduced would be probably less than 0.1%. In order to reduce the second objection as far as possible, two volumetric flasks were calibrated and the air in them was dried by standing over sulfuric acid. The air was displaced subsequently by sulfuric acid. This caused no appreciable change in results. (4) We have already mentioned the difficulties in titration. All of the buret readings were checked by at least two observers. The error in titration is undoubtedly great at the lower temperatures studied. (5) Any lack of saturation of the gas with the vapor would make our results too low. The rate of flow was varied by a factor of nearly four, and only with the most rapid rate of flow used did there seem to be any indication that the gas was not saturated. (6) The temperature of the thermostat was read by means of a thermometer calibrated by the Bureau of Standards. The thermometer was calibrated only at the 10° intervals, so that temperatures other than those in the immediate neighborhood of the 10° marks would be less accurately known. The temperature of the thermostat remained constant to about 0.1°, except at the highest temperature used (105°) for which considerably less variation was noted. Since the temperature coefficient of the vapor pressure is rather high, lack of constancy would introduce an appreciable error. (7) The vapor pressures are calculated by means of the perfect gas law, $pv = nRT$. The assumption of the perfect gas law at such low pressures would seem to be justified. The increase in volume of the gas due to the presence of the vapor was determined from the approximate value of the vapor pressure and this corrected volume used in the calculations. The correction amounted to less than 0.1% even at the highest temperature used. The results should be accurate to about 2%, except at the lowest temperature studied (60°). All of the points obtained after the procedure described was adopted are given in Table I, with the exception of one point which was about 50% too low due to the fact that some of the acid had been decomposed in sealing off the tube at the end of the run.

Only those values obtained after the final procedure was adopted are given in the table. Some of the earlier values (for which the U-tube

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[5] Landolt-Börnstein-Roth-Scheel, "Tabellen," Julius Springer, Berlin, 1923, p. 114.

Table I

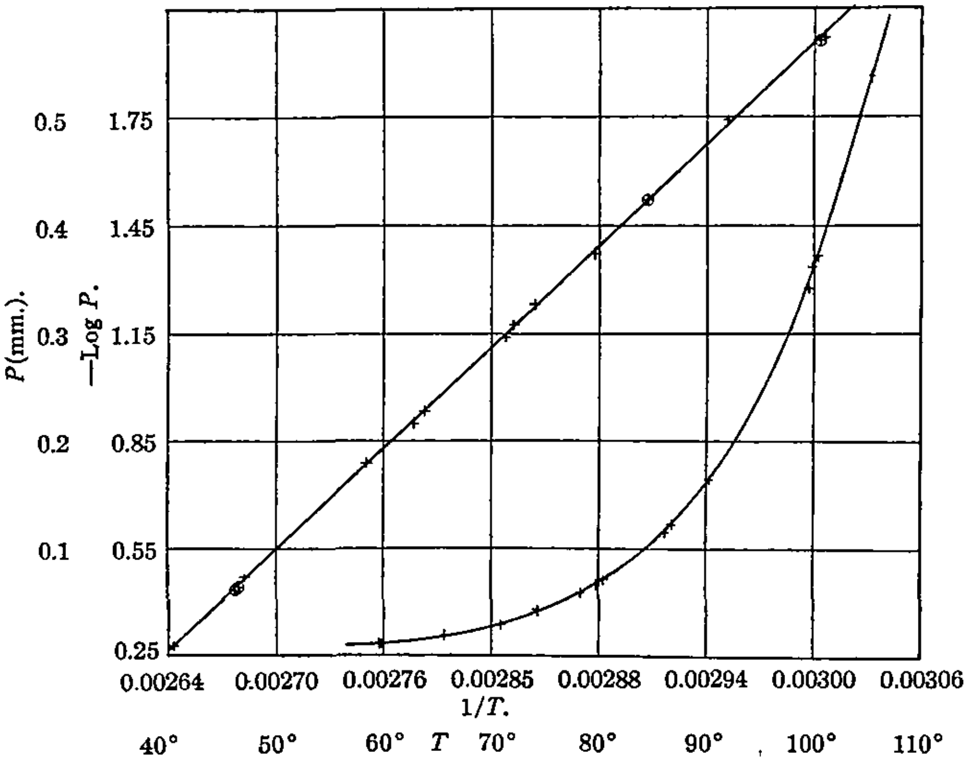
Results

Temp., °C. ±0.1°	Approx rate of flow, L. per hour	Vol. of dry air at temp. of thermostat, Liters	0.009194 N $KMnO_4$, cc.	P, mm.	P (calcd.)
59.55	0.78	20.27	1.15[b]	0.0108	0.0103
65.65	1.72	22.69	4.28	.0183	.0186
74.40	1.76	17.59	7.51	.0426	.0417
78.40	2.7	5.966	3.48	.0588	.0596
79.82	0.93	12.07	8.02	.0672	.0676
80.50	0.73	9.747	6.94	.0722	.0716
86.17	2.44	6.105	3.44[b]	.1161	.1164
86.90	2.19	12.07	7.18[b]	.1236	.1234
90.31	1.22	10.06	15.88	.1645	.1643
99.49	0.74	3.042	9.72	.3412	.3437
105.28[a]	1.42	5.219	25.88	.5374	.5374

[a] ±0.03°.

[b] 0.01838 N $KMnO_4$ used.

immersed in ice was not used) agree well with those given, particularly if the rate of flow is small, or the temperature high. Thus a preliminary value at 59.80° gave 0.0109, calcd. 0.0106. The values in the column marked "calcd." are obtained from the equation $\log p = -(4726.9499/T) + 12.22292$. This equation was obtained by making a large scale plot of



Points in circles are preliminary in character.

the logarithm of the pressure against the reciprocal of the absolute temperature and drawing the best straight line through the points, giving somewhat more weight to the points obtained at higher temperatures. The agreement is within 2% except at the lowest temperature used. Since this equation fits the data as well as any other type of equation we tried, the heat of vaporization must be very nearly constant at 21,650 calories per mole. It is very difficult to estimate with accuracy what the specific heat of the vapor should be. It would undoubtedly be higher than that of ethane, which also has eight atoms in the molecule. The specific heat of solid anhydrous oxalic acid has been determined by Nernst, Koref and Lindemann,[6] who find 25.07 calories per mole for the interval 3° to 47°. The specific heat of solid acetic acid is much higher (about 37).[7] By use of the equation given by Henglein[8] for the vapor pressure of glacial acetic acid it is found that ΔC_p is about 4.5 calories between 0° and 50°. If 29 is taken as an average specific heat per mole for liquid acetic acid over this range, the specific heat of the vapor would be about 24.5 calories per mole. This result would make it appear that it might not be unreasonable to expect a small value of ΔC_p for the vaporization of solid oxalic acid. Since the heat of sublimation is very high, one might expect, therefore, an equation of the type used to fit the data fairly well.

Extrapolation of this equation gives a value differing but slightly at 150° from the values obtained by means of more complicated equations.

Summary

1. The vapor pressure of solid anhydrous oxalic acid has been determined between 60° and 105°.

2. The values are found to be satisfactorily represented by the equation $\log p = -(4726.9499/T) + 12.22292$.

3. It may not be unreasonable to expect the specific heat of the vapor to be only slightly different from that of the solid. The heat of sublimation as given by the equation would be 21,650 calories per mole.

CHICAGO, ILLINOIS

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[6] Ref. 5, p. 1271.

[7] Ref. 5, p. 1269.

[8] Henglein, *Z. physik. Chem.*, 98, 1 (1921).

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE DIELECTRIC CONSTANTS OF BINARY MIXTURES

BY JOHN WARREN WILLIAMS AND IGNACE J. KRCHMA

RECEIVED APRIL 20, 1926 PUBLISHED JULY 6, 1926

The introduction of the "vacuum" or "three-electrode" tube has made possible several accurate methods for the measurement of the dielectric constant. These measurements serve to test the newer theories of atomic structure[1] in the case of the pure non-conducting liquids, and the later theories of electrolytic solutions[2] in the case of conducting systems.

The determination of the dielectric constants of several binary mixtures was undertaken, and in this paper are presented the results on mixtures of benzene and toluene, chlorobenzene and bromobenzene, and carbon tetrachloride and benzene. The dielectric constants of the components of these solutions were also determined and are included in the tables. It has been shown[3] that few solutions, if any, are strictly ideal. The results here presented are in agreement with that conclusion.

Method

The method used for the determination of the dielectric constant of the liquids was one of the so-called "electrical resonance methods."[4] It does, however, contain several novel features.

A diagram of the apparatus used is shown in Fig. 1. In the first circuit oscillations are generated by an electron tube in a so-called Hartley circuit. The grid and filament of the tube in this particular circuit are connected to the branched circuit containing inductance, L_1, and capacitance, C, which constitute the oscillatory circuit. The fundamental constituent of the waves generated in this circuit may be changed at will to any desired frequency by adjustment of the capacity in the circuit, and made to equal that of the second circuit.

Circuit No. 2 may be described as a regenerative receiving circuit. It consists of a simple wave-meter circuit containing inductance and capacitance, with a two-stage amplifier, inductively coupled, connected in series. The circuit is caused to oscillate by means of the "Feed Back Regeneration" principle. This oscillation is maintained constant, great care being taken to prevent variations in batteries, inductance and capacitance in the circuit. The telephone receivers are connected in series in the plate cir-

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[1] Lewis, "Valence and the Structure of the Atom," Chemical Catalog Company, New York, **1924**.

[2] Debye-Hückel, *Physik. Z.*, **24**, 185 (1923); **25**, 145 (1924).

[3] Williams and Daniels, THIS JOURNAL, **47**, 1490 (1925).

[4] Hyslop and Carman, *Phys. Rev.*, **15**, 243 (1920). Waibel, *Ann. Physik*, **72**, 161 (1923). Fritts, *Phys. Rev.*, **23**, 345 (1924), and others.

cuit of the second vacuum tube. This circuit then acts as both an oscillatory circuit and receiving circuit, thereby eliminating a third circuit which is generally employed for the reception of the beats in the usual heterodyne method for the measurements of capacities.

The dielectric container, C_x, which is used for the determination of the dielectric constant of the liquid is connected in parallel with condenser, C_1, of Circuit 1. C_1 consists of two standard variable air condensers connected in parallel. One was manufactured by the Leeds and Northrup Company of Philadelphia and the other is a Standard Precision Condenser (Type 222) made by the General Radio Company of Cambridge, Massachusetts. The dielectric cell was especially designed for the purpose in hand and constructed in the University of Wisconsin Shops. It is contained in a Pyrex glass vessel and is fitted with a hard rubber cover. External to the dielectric cell is a perforated copper container which is bolted to a thermostat, thus allowing the water of the thermostat to circulate about the cell. This copper container serves as a shield to protect the condenser from stray capacity effects. The depth of the cell is such that the plates of the condenser are remote from any ungrounded metallic portions of the cell cover. The variable condensers are carefully grounded and shielded to prevent external capacity effects.

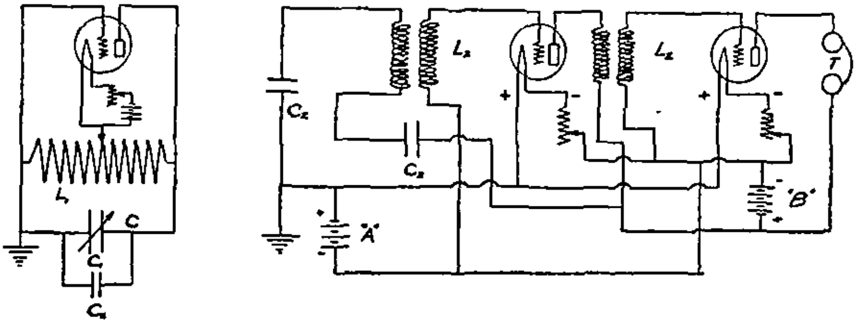

Fig. 1.

The dielectric constant of a liquid is determined as follows. The filaments of the vacuum tubes in both circuits are lighted from isolated sets of storage batteries, the current being carefully maintained constant by means of suitable rheostats. Circuit 2 is caused to oscillate by increasing the plate current in the tubes until regeneration begins. The circuit is now maintained perfectly constant so that the waves generated have a constant frequency. Circuit 1 is now adjusted to this frequency by means of condensers, C_1. The dielectric cell, C_x, is connected in the circuit at all times. The position of resonance just mentioned is determined with the plates in air and set at a definite and perfectly reproducible position, which may be called "A." The plates are now adjusted to a position "B" and the circuit is again brought to resonance with the constant Circuit 2. The difference in capacity of the dielectric cell in air with the plates in these two positions is determined by means of the calibrations of the standard condensers in C_1. The difference in capacity between these positions, A and B, of the dielectric cell with the plates immersed in the liquid whose dielectric constant is to be measured is now determined. The dielectric constant of the liquid is then calculated by dividing the difference in capacity between positions A and B when the plates are immersed in the liquid by the difference in capacity in air between these positions. The dielectric cell is so constructed that a number of settings may be used for each liquid, making check determinations easy to obtain. These measurements may be made easily and very rapidly. This method entirely eliminates any correction for the capacity of the leads, etc., a distinct advantage since these capacities, though small, are uncertain, and should be avoided for accurate determinations.

The accuracy and consistency of the measurements are illustrated by fifteen consecutive observations made on benzene at 25° which gave a mean value of 2.282, with an average deviation from the mean of ± 0.0025, and a maximum deviation from the mean of 0.004.

Purification of Materials

Benzene.—The benzene, obtained from the Eastman Kodak Company, was shaken with concd. sulfuric acid, washed with dil. sodium hydroxide solution and with distilled water. It was frozen out twice and fractionated, and showed no blackening with mercury. The drying agent used was phosphorus pentoxide. The liquid gave practically the same physical constants that are given by Richards and Shipley.[5]

Toluene.—This material was obtained from the Mallinckrodt Chemical Works. It was shaken with concd. sulfuric acid, washed with dil. sodium hydroxide and distilled water. After standing over mercury for a week it was dried with phosphorus pentoxide and fractionated.

Carbon Tetrachloride.—The preparation (obtained from Merck and Company) was refluxed over mercury and washed with concd. sulfuric acid to remove sulfides. It was then washed with dil. sodium hydroxide solution and water, dried over fused calcium chloride and fractionated.

Chlorobenzene.—This material was obtained from the Eastman Kodak Company. It was carefully dried and fractionated.

Bromobenzene.—The liquid was also obtained from the Eastman Kodak Company. It was treated as was the chlorobenzene.

Experimental Results

The dielectric constants of benzene, toluene, carbon tetrachloride, bromobenzene and chlorobenzene at 25° were obtained. In all cases the frequency was of the order 10^6 cycles per second. The dielectric constant of air was taken as unity.

The results on systems of benzene-toluene, benzene-carbon tetrachloride and bromobenzene-chlorobenzene are summarized in Table II and in Figs.

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[5] Richards and Shipley, THIS JOURNAL, **41**, 2022 (1919).

TABLE I

DIELECTRIC CONSTANTS AT 25°

Liquid	Dielectric constant	B. p., °C.
Benzene	2.282 ± 0.0020	80.10– 80.15
Toluene	2.378 ± .0030	110.60–110.80
Carbon tetrachloride	2.230 ± .0030	76.45– 76.52
Bromobenzene	5.397 ± .0050	156.20–156.30
Chlorobenzene	5.610 ± .0050	131.85–132.15

2, 4 and 5, where percentage composition is plotted against dielectric constant.

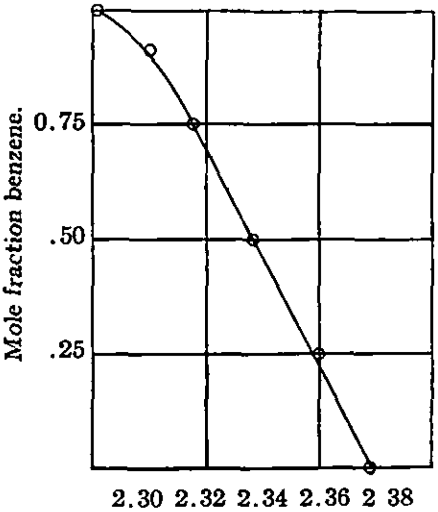

Fig. 2.—C_6H_6—C_7H_8.

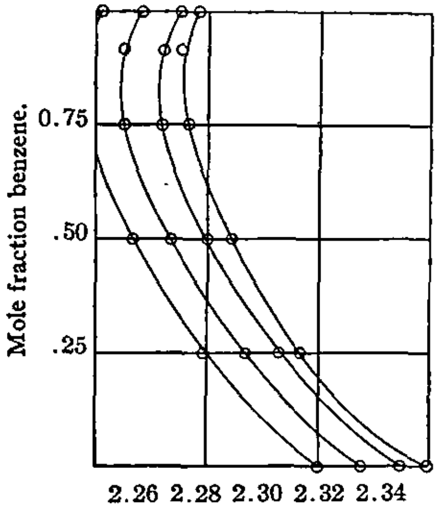

Fig. 3.—C_6H_6—C_7H_8. Grützmacher.

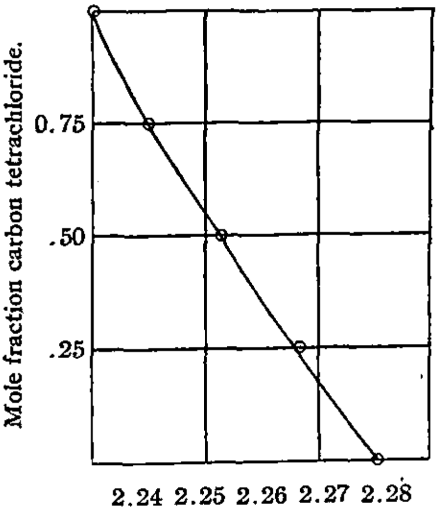

Fig. 4.—C_6H_6—CCl_4.

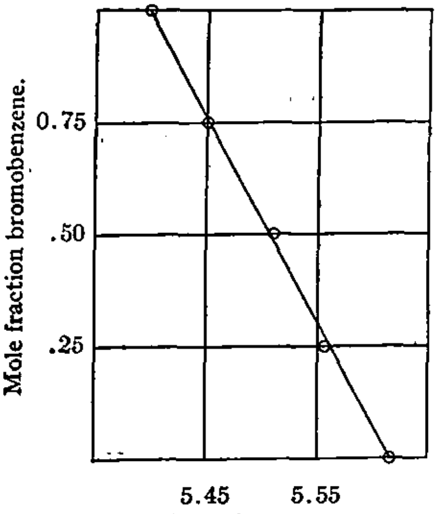

Fig. 5.—C_6H_5Cl—C_6H_5Br.

Discussion of Results

A. Pure Liquids

Concerning the dielectric constants of the pure liquids, it may be stated that with the exception of chlorobenzene the values obtained are in good agreement with the commonly accepted values. For example, in the case of benzene Turner[6] obtained 2.289 ± 0.003 at 18°. Since $\frac{d\,(D.C.)}{dt} =$ —0.001 (approximately), his value at 25° would be 2.282.

The dielectric constant of chlorobenzene is decidedly different from that reported by Veley.[7] This author reports a value of 10.95 at 10.8°, which has been accepted by the Landolt-Börnstein "Tabellen" and has been used in many theoretical discussions, for example, by Hildebrand.[8] It is hard to understand why chlorobenzene should have such a radically different dielectric constant from bromobenzene (5.397) and iodobenzene[8] (4.6), especially since other physical properties such as specific heat, molecular refraction, molecular volume, etc., show periodic changes as bromine and iodine are substituted in place of chlorine.

Table II

Dielectric Constant—Composition Data for Mixtures at 25°

Mole fraction A[a], %	Benzene-toluene					Benzene-carbon Tetrachloride			Bromobenzene-Chlorobenzene		
		Dielectric constant					Dielectric Constant			Dielectric Constant	
	n_D^{25}	Obs.	Dev.	Grützmacher	Dev.	n_D^{25}	Obs.	Dev.	n_D^{25}	Obs.	Dev.
100	1— 49780	2.282	.....	2.277	.....	1.— 49780	2.282	.....	1— 55711	5.397	.....
91.5	49724	2.304	+0.014	2.271	−0 013	...	...	.....	...	...	.....
75	49649	2.315	+ .008	2.273	− .026	48770	2.267	−0 002	54874	5.448	.... .
50	49653	2.337	+ .007	2 289	− 031	47766	2.253	− .003	54059	5.510	+0.006
25	49460	2 362	+ .006	2.314	− .027	46747	2.240	− .003	53179	5.557	− .002
0	49392	2.378	....	2.360	.....	45724	2.230	.....	52343	5 610	.....

[a] In each case the first named component is designated by A.

Again, data on chlorobenzene-bromobenzene mixtures (vapor-pressure relations, heats of mixing and volume changes) by Young[9] and specific heat relations[3] lead to the conclusion that this system is at least approximately ideal, but if the dielectric constant of chlorobenzene were over twice that of bromobenzene (as previously given) it would have been expected that the various physical constants for these solutions would show greater deviations from those calculable on the basis of Raoult's law, since it has been suggested by Kendall,[10] and by Hildebrand[8] that the dielectric constant may be considered as being the most direct evidence of polarity

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[6] Turner, *Z. physik. Chem.*, **35**, 385 (1900).

[7] Veley, *Phil. Mag.*, [6] **11**, 73 (1906).

[8] Hildebrand, "Solubility," Chemical Catalog Company, New York, **1924**, pp. 89–90.

[9] Young, *J. Chem. Soc.*, **81**, 768 (1902).

[10] Kendall, This Journal, **39**, 2323 (1917).

or association in a liquid, and since association in a liquid is usually (though not always[3]) a cause for the formation of a non-ideal solution.

The value obtained, 5.610 at 25°, for chlorobenzene was carefully checked and samples of the material from several different sources were used, giving the same results within the limits of experimental error. The final samples used had considerably better physical constants than those of the chlorobenzene described under purification of materials and used for the binary mixtures. It was necessary to use larger quantities for them, and it was not practicable to confine the distillate to very narrow ranges.

B. Binary Mixtures

The binary mixtures were studied with the purpose of continuing the study of the thermodynamics and the mechanism of solutions.[3] An attempt has been made to account for the deviations from the ideal solution by a study of the dielectric constants of certain mixtures, since that property has been considered to be the most direct evidence of association or polarity. In general, a polymerized molecule has a greater electrostatic moment than the simple molecule.[11] This means that the dielectric constant of the solvent will be greater in its associated state, and if a de-association takes place on solution, the dielectric constant of that component in solution will be less than that of the pure liquid. And, conversely, if two liquids unite chemically the electrostatic moment of the molecules will very probably be increased and the forces holding the electric charge will be weakened, causing the dielectric constant of a component to be greater in solution than in its pure state.

On this basis it should be possible to predict whether the dielectric constant of a solvent in solution will be greater or less than that of the pure solvent. However, the problem is not simple, and it has already been shown[3] that in some cases there are at least two simultaneous reactions taking place when liquids are mixed—a de-association of the liquids and a combination between the two liquids. These factors lead to opposing tendencies in any physical property. It is not possible with the data here presented to do more than point out in a qualitative way the factors which are operating for the binary mixtures studied.

With these general considerations in view, a brief discussion of each of the three systems studied will be given.

Benzene-Toluene.—The dielectric constants for solutions of benzene and toluene over a considerable range of temperature have recently been determined by Grützmacher.[12] If we determine (by graphic interpolation of his data) the values of the dielectric constants at 25°, 30°, 40° and 50°, of the various solutions examined by this investigator and plot dielectric

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[11] Creighton and Fink, "Electrochemistry," Wiley and Sons, Inc., New York, **1924**, Vol. I, pp. 58–59.

[12] Grützmacher, *Z. Physik*, **28**, 342 (1924).

constant-composition curves for these values, curves shown in Fig. 3 are obtained. It will be noted from these curves that there is a distinct minimum in the dielectric constant at 85 mole fractions benzene, 15 mole fractions toluene, and that over the whole range of composition the dielectric constants as determined are considerably less than those which would be calculated, assuming an ideal solution.

The results obtained in this investigation have already been presented. It will be noted (Fig. 2) that the dielectric constants of all mixtures lie between those of the two components, and that in solutions in which the benzene content is less than 0.75 mole fraction the points lie practically on a straight line. It was evident from the slope of this line, however, that the extrapolation to 1.00 mole fraction benzene would not give the previously determined value for pure benzene. Therefore it was necessary to determine the dielectric constant of a 0.915 mole fraction benzene-0.085 mole fraction toluene solution to complete the curve. Since all points on the curve were determined with a mean possible error of not greater than ± 0.0025 it is believed that the deviations of the observed results from those calculated using Raoult's law and presented in Table IV are significant. It will be evident from the curves and the table that these values are hard to reconcile with those of Grützmacher. After the first curve had been constructed the values of Table II for the solutions were redetermined. Very pure benzene and toluene were finally and thoroughly dried over metallic sodium, and the dielectric constants of the mixtures determined immediately. In all cases the previous values were verified within the limits of experimental error. The value of the 0.915 mole fraction benzene-0.085 mole fraction toluene solution was repeatedly checked to ± 0.002.

From previous measurements of the physical properties of benzene-toluene solutions large deviations from the law of ideal solutions are not to be expected. Fig. 2 and Table II show this to be true in the case of their dielectric constants. The deviations are significant, however, especially in the case of the 0.915 mole fraction benzene-0.085 mole fraction toluene solution. In the previous paper of this series,[3] it was shown that in the higher concentrations of benzene, the partial molal heat capacity of the benzene in solution was less than the molal heat capacity of the pure benzene, and that the partial molal heat capacity of the benzene increased as its mole fraction decreased. The results on the dielectric constants of the mixtures constitute an excellent check on these results, for the deviations from the ideal solution exactly parallel to those of the heat capacity relations. In the more concentrated benzene solutions the dielectric constant of the benzene in solution is greater than that of the pure liquid and this quantity becomes less as the concentration of the benzene is decreased.

It does not seem probable that the dielectric constants of benzene-toluene solutions should deviate so much from those calculated on the basis of Raoult's law as is required by the data given by Grützmacher.[12] Neither does it seem probable that this deviation should be greatest in the region of equal molal fractions of the components, since measurements of other physical properties show that solutions, with the exception of those in which the mole fraction of benzene is high, behave in a manner which approaches that of the ideal solution.

Benzene-Carbon Tetrachloride.—Systems of these components have been subjected to many physicochemical studies. They show for the most part deviations from "ideality" corresponding to a slight de-association of complex molecules, although the data are somewhat conflicting. From the measurements of vapor pressure,[13,14] heats of mixing[15] and specific heats[3] it has been suggested that association has been diminished on solution.

It is evident from Table II that the solutions show a slight deviation from the ideal condition as regards their dielectric constants. The fact that these observed dielectric constants are slightly less than those calculated on the basis of Raoult's law tends to indicate that association has been diminished and the number of molecules increased since the observed values are consistently less than the calculated ones. However, the magnitude of the deviations is so small that it is hardly possible to draw any definite conclusions as to what happens on solution.

Chlorobenzene-Bromobenzene.—The results of the measurements on this system, as summarized in Table II, indicate that chlorobenzene and bromobenzene form solutions which are ideal within the limits of experimental error, a conclusion which Young[9] arrived at from measurements of vapor pressure, heats of mixing and volume changes.

The value obtained for the dielectric constant of chlorobenzene has been discussed. This new value makes it probable that only slight deviations from the ideal solution for any physical property of these solutions may be expected. The dielectric constants of the components are comparatively high, which is considered to be evidence of polarity or association, but it has been pointed out[3] that the mere existence of association in a pure liquid is not a sufficient cause for the formation of a non-ideal solution.

Conclusions

The study of the causes of deviations of physical properties of solutions from Raoult's law has been discussed by Hildebrand.[16] The results here presented confirm the impression given that the changes taking place on solution are intricate indeed. The study is being extended to other solutions which it is hoped will give more definite evidence for either one or

[13] Zawidski, *Z. physik. Chem.*, **35**, 129 (1900).

[14] Dolezalek, *ibid.*, **64**, 727 (1908).

[15] Young and Fortey, *J. Chem. Soc.*, **83**, 45, 68 (1903).

[16] Ref. 8, Chap. 7.

the other of the two fundamental factors which are being recognized in explaining the properties of solutions, namely, the formation of compounds, and the breaking down of complex molecules present in the liquids.

Summary

1. An electrical resonance method, making use of several novel features, for the determination of the dielectric constants of liquids has been presented.

2. The dielectric constants at 25° of pure benzene, toluene, carbon tetrachloride, bromobenzene and chlorobenzene have been redetermined. A new value, and it is believed a more exact one, has been found for chlorobenzene.

3. The dielectric constants of three binary mixtures at 25° have been determined at various concentrations. The systems studied are benzene-toluene, benzene-carbon tetrachloride and chlorobenzene-bromobenzene, all of which may be considered as being nearly ideal solutions.

4. Each of the systems studied has been critically discussed, and an attempt made to explain the nature of the changes taking place on solution, from a consideration of values of the dielectric constants of the solutions.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS, UNITED STATES DEPARTMENT OF COMMERCE]

THE RATE OF FLAME PROPAGATION IN GASEOUS EXPLOSIVE REACTIONS[1]

BY F. W. STEVENS

RECEIVED APRIL 30, 1926 PUBLISHED JULY 6, 1926

In the case of gaseous explosive reactions the energy transformation of the chemical system is brought about by the spatial propagation within the explosive gases of a thin, sharply defined area of reaction marked by flame.[2] The expression, then, rate of flame propagation, should refer to the linear rate of displacement of this area relative to the active gaseous components in which it propagates itself. This rate may be expressed by

$$s = v_p/ta \qquad (1)$$

where v_p is the volume at constant pressure of the active components passing an element of the flame front in time t; a is the area of this element.[3,4,5,6]

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[1] Published by permission of the Director of the National Bureau of Standards of the U. S. Department of Commerce.

[2] Luther, *Z. Elektrochem.*, **12**, 597 (1906).

[3] Bunsen, *Phil. Mag.*, **34**, 1 (1867).

[4] Gouy, *Ann. chim. phys.*, [5] **18**, 18 (1879).

[5] Michelson, *Ann. Phys. Chem.*, **37**, 1 (1887).

[6] Mache, "Die Physik der Verbrennungserscheinungen," Viet and Co., Leipzig, 1918.

Haber[7,8] recognizes three well-defined zones in the progress of a gaseous explosion: the region occupied by the explosive gases within which the zone of reaction, marked by flame, propagates itself; the region of the flame within which the explosive reaction is initiated and, for the conditions there prevailing, completed; and the region occupied by the equilibrium products of the reaction behind the flame. "This region," he states, "is not, from a thermodynamic standpoint, free from oxygen, but from an analytical standpoint it is. In this region no further burning takes place." The expression for this equilibrium condition is given by the equilibrium constant,

$$K = \frac{[\mathrm{A}]^{n_1}\,[\mathrm{B}]^{n}\,[\mathrm{C}]^{n_3}}{[\mathrm{A}']^{n'_1}\,[\mathrm{B}']^{n'_2}\,[\mathrm{C}']^{n'_3}} \tag{2}$$

It is found possible by other devices than a burner so to condition a gaseous explosion that these zones shall maintain, during the explosive reaction, definite geometrical forms and relative positions of symmetry, with a high degree of precision. With especial reference to the rate of flame propagation in explosive gaseous reactions, it is the purpose of this paper to describe a simple device and method based largely upon this symmetry and found applicable both to thermodynamic and kinetic studies of the explosive gaseous reaction. Both the method and device to be described are the direct outgrowth, as will be seen, of the important series of thermodynamic studies begun by Langen[9] and extended by Pier,[10] Bjerrum,[11] and Siegel,[12] in which the gaseous explosive reaction was first successfully employed as a method of precision to determine the specific heat of gases at high temperatures; also to determine the degree of dissociation over wide ranges of temperature and pressure; of the important products of combustion, carbon dioxide and water vapor. The accuracy of the experimental method developed by these investigators depends in large part upon so conditioning the explosive reaction that the heat losses during the process shall be reduced to a minimum. The device employed by them was a spherical bomb of constant volume fired from the center. By this arrangement the three zones mentioned by Haber are maintained concentric with the spherical bomb throughout the reaction; the central sphere of equilibrium products originating at the center is thus protected from heat losses due to conduction and convection until the end of the reaction when the flame area that encloses them reaches the walls of the bomb. In case the flame movement within the bomb has not been more rapid than the rate of pressure distribution within the gases, a Pier manometer at

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[7] Haber, *Z. physik. Chem.*, **68,** 726 (1909).

[8] Hiller, *ibid.*, **81,** 591 (1912).

[9] Langen, *Mitt. Forsch. arbeit.*, **8,** 1 (1903).

[10] Pier, *Z. Elektrochem.*, **15,** 536 (1909).

[11] Bjerrum, *Z. physik. Chem.*, **79,** 513 (1912).

[12] Siegel, *Z. physik. Chem.*, **87,** 641 (1914).

the surface of the bomb registers the maximum pressure at the completion of the reaction. This pressure is identified with the equilibrium condition of the reaction products (Equation 2) and, as Siegel has shown for the case of such trimolecular reactions as $2CO + O_2$ and $2H_2O + O_2$, it is identified with the degree of dissociation, x, of the combustion products.

$$K = \frac{[CO]^2\,[O_2]}{[CO_2]^2} = \frac{x^3}{(1-x)^2\left(1+\frac{x}{2}\right)} \times \frac{P}{2RT} \quad (3)$$

Although these investigations were concerned with the thermodynamics of the reaction, the reaction rate was, nevertheless, always a major factor in the practical application of the method and determined its limitations.

Since it was assumed that the readings of a manometer—at least for moderate explosion rates—could give a reliable time-pressure record of the reaction, this, in connection with the fact that the area of reaction assumed the form of an expanding spherical shell concentric with the bomb, led to numerous involved attempts to deduce from the time-pressure record of a manometer the movement of the flame within the bomb.[13,14]

Since these theoretical deductions were unrelated to the principles of chemical kinetics and lacked direct experimental proof, the writer attempted to follow the flame movement within the bomb by making use of the photographic method developed by Dixon[15] in his work on flame movement within cylindrical containers. A spherical bomb of glass was used instead of steel. This device proved unsatisfactory although experience with it was convincing of the futility of the use of manometric methods in connection with time intervals approaching those met with in the study of sound phenomena, as is the case when resonance or impact waves develop within the bomb.

An attempt was then made to use a soap film container fired from the center. The use of this simple and easily manipulated device in connection with photographic methods revealed not only the accurate symmetry maintained by the transforming zones during the reaction, shown in Fig. 3, but showed also that at constant pressure, the rate of flame propagation within the explosive gases remains constant during the reaction. A constant rate of supply at a constant concentration of the active components to the flame area would seem to indicate the maintenance of a constant condition within or a constant gradient across the zone of reaction as well as a constant equilibrium condition of the reaction products leaving the flame. The photographic records show only a decrease in the volume of equilibrium products after the flame has passed.

This device, for explosion rates not too near the velocity of sound in the

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[13] Nägel, *Mitt. Forsch. arbeit.*, 54, 1 (1908).

[14] Flamm und Mache, *Akad. Wien. Ber.*, [IIA] 126, 9 (1917).

[15] Dixon, *Phil. Trans.*, R. S., 200, 315 (1903).

gases, functions as a bomb of constant pressure[16] and in this respect provides the complement to the bomb of constant volume. For a study of a number of explosive gaseous reactions it has the advantage over a bomb of constant volume of dispensing with a manometer; of maintaining constant the concentrations of the explosive gases the flame is entering till the end of the reaction; and, being transparent, it permits a direct and accurate photographic time-volume record of the reaction to be secured; whereas a time-pressure record sought by the use of a manometer involves indefinite changes in the concentrations of the gases due to inconstant pressure during the reaction.

The bubble device also readily permits the effect of pressure upon the rate of flame propagation to be observed. For this purpose it is enclosed within a sufficiently large and strong air-tight chamber also of spherical form, where the reaction may run its course at a pressure practically constant either below or above atmospheric.

A number of simple gases, together with mixtures of simple gases both active and inert, have been investigated during the past few years by the method more fully described below. Besides other interesting characteristics of flame behavior, a study of the photographic time-volume records obtained has shown that a definite relation exists between the movement of the flame area and the initial concentrations of the active gaseous components within which it propagates itself. This relation may be expressed as

$$\dot{s} = \frac{v_p}{ta} = k_1\,[\mathrm{A}]^{n_1}\,[\mathrm{B}]^{n_2}\,[\mathrm{C}]^{n_3} \tag{4}$$

where k_1 is a proportionality factor. The experimental results offered to illustrate this relationship are drawn from a study of the explosive reaction

$$2\mathrm{CO} + \mathrm{O_2} \rightleftharpoons 2\mathrm{CO_2} \tag{5}$$

at water-vapor saturation and at atmospheric pressure.

Experimental Part

A bubble, *b*, see Fig. 1, of convenient size, is blown with a mixture of the explosive gases, carbon monoxide and oxygen, whose partial pressures are known. Through the aperture from which the bubble is blown is inserted an ignition gap *c* to the center, as near as may be, of the bubble. Back of the bubble is placed a black, opaque screen, *o*, *o*, provided with a narrow horizontal slit that can be illuminated. This slit falls in the same horizontal plane as *c*. A camera whose sensitive film is attached to a rotating drum *f*, is focused on *c* and the outlying edges of the bubble at either side of *c*. While the drum is at rest and the translucent slit illuminated, an exposure is made securing a silhouetted image of *c* and the edges of the bubble. This record compared with the photographic record of a milli-

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[16] Nat. Advisory Committee for Aeronautics, Rept. No. 176 (1923).

meter scale in the same position gives the diameter of the sphere of explosive gases to be considered—and this irrespective of the actual shape of the bubble which is never a sphere. A record showing the appearance of this dimension is shown at 7 and 8, Fig. 2. The illumination behind *o*, *o*, is now turned off; the drum *f*, bearing the photographic film, is set in rotation, the cap of the camera removed and an ignition spark passed. The record of this spark on the photographic film marks the center of the spherical, expanding area of reaction. Only the horizontal motion of this flame area is allowed to reach the photographic film. This is accomplished by interposing between the lens and as close as possible to the photographic film, a second screen, *s*, with a narrow horizontal aperture. The horizontal motion of the flame area and the motion of the photographic film are at right angles to each other so that the flame trace on the film is the resultant of these two motions. The inclination of the flame trace to the horizontal gives the velocity of the flame movement *in space* at any instant during its progress—provided the velocity of the film during the reaction is known. The velocity of the film during the explosion is determined in the following way: The narrow aper-

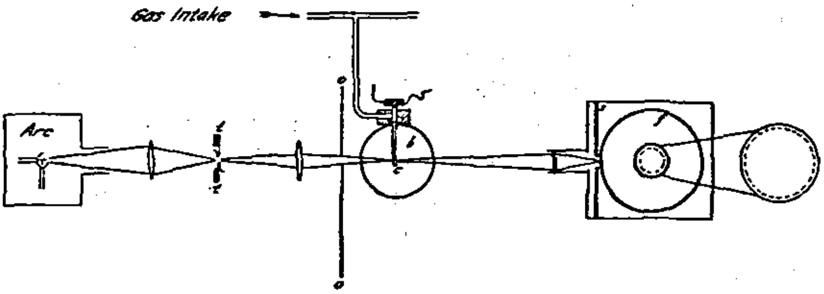

Fig. 1.—The arrangement of apparatus: *b*, bubble holding explosive gases; *c*, ignition gap; *o*, screen; *t*, tuning fork with shutters; *f*, rotating drum carrying sensitive film; *s*, screen with narrow horizontal opening.

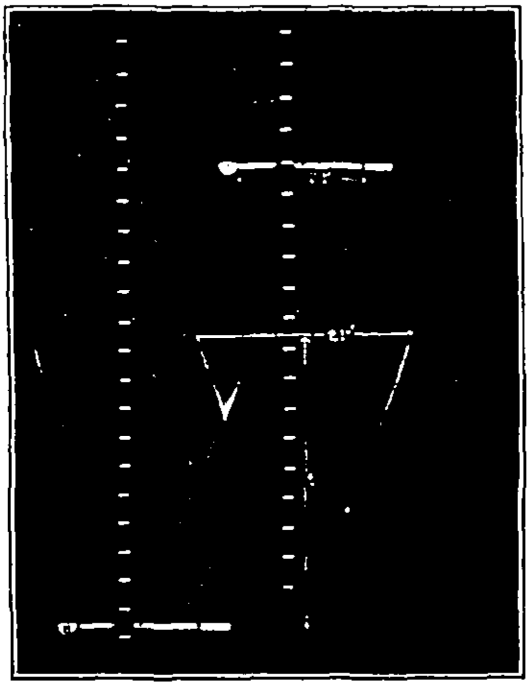

Fig. 2.—A photographic record of two observations of the same explosive gases; $2r$, initial diameter of gaseous sphere before reaction; $2r'$, final diameter of gaseous sphere at instant reaction is completed; t, interval of reaction.

ture in the shutters of a calibrated tuning fork, *t*, *t*, is placed at one side of and close to the optical axis of the camera passing through *c*. This aperture is brightly illuminated by an arc. An image of this illuminated aperture is formed in space at one side of and in the same vertical plane as *c*. When the fork is vibrating this image is intermittent at twice the normal frequency of the fork. These flashes are recorded on the rotating sensitive film during the progress of the explosive reaction. A device attached to the drum of the camera prevents the time record continuing longer than one revolution of the drum.

The diameter of the gaseous sphere of initial components considered is given by the photographic record $2r$, Fig. 2; the final diameter of the sphere of equilibrium products, by $2r'$. Since the velocity of the flame, under the condition of constant pressure, is constant, its velocity *in space*, s', may be found at any convenient position on the photographic record between the initial and end-point of the reaction. At the end of the reaction its value may be expressed in terms of r',

$$s' = r'/t \tag{6}$$

The velocity, s, of the flame relative to the explosive gases in which it is propagated, is given for the case where the zone of reaction is an expanding spherical shell, by

$$s = \frac{v_p}{ta} = s'\frac{r^3}{r'^3} = \frac{r^3}{r'^2 t} \tag{7}$$

Results

The value of s was determined by the method described for a large number of different partial-pressure combinations of the gases carbon monoxide and oxygen at water-vapor saturation. These values covered practically the entire range of mixtures of these gases that would ignite. Fig. 3, by the solid circles, expresses graphically the relation between the rate of flame propagation within the gases and the corresponding initial partial pressures of their active components. The graph readily suggests a distribution curve; and since the results show that the rate of propagation of the zone of reaction with the explosive gases is related to their concentrations, a trial was made to see whether this rate was proportional to the product of their concentrations.

$$s = k_1\,[\mathrm{CO}]^2\,[\mathrm{O}_2] \tag{8}$$

In order to test this expression, the experimental values of s together with the corresponding partial pressures of the active gases were arranged as shown in Table I.

The value of k_1 is shown by the photographic records to remain constant during each reaction. It is shown by the table to remain fairly constant over the entire range of mixtures of the gases that will ignite. Using the average value of k_1 as given in the table to compute s in the expression

TABLE I

OBSERVED FLAME VELOCITIES OF THE CO, O_2 EXPLOSIVE REACTION

Record No	Partial pressure [CO]	[O_2]	$s' = \frac{r'}{t}$ cm /sec	$s = s' \frac{r^3}{r'^3}$ cm /sec	Mean value S	$k_1 = \frac{s}{[CO]^2 [O_2]}$
1	0 241	0.759	126	31 7		
2			127	30 7		
3			131	30 8	31 1	703
15	305	695	282	41 6		
16			289	41 55	41 6	643
2′	357	643	415	57 7		
3′			419	59 2		
4′			393	58 9	58 6	715
4	380	620	418	61 9		
5			418	61 9		
6			418	61 4		
7			421	62 4	61 9	691
8	453	547	520	78 1		
9			491	80 8		
10			510	77 4	78 8	702
11	500	500	593	88 0		
12			590	88 8		
12′			590	87 8	88 2	705
13	564	.436	694	94 8		
14			678	96 8		
15′			705	98 3	96 6	696
45	.648	352	700	99 6		
46			727	103 0		
47			718	103 5		
48			740	105 0	102 8	697
42	668	.332	687	105 0		
43			731	104 0		
14′			730	103 5		
16′			785	103 3		
17			769	103 0		
18			785	103 3		
19			777	106 0	104	702
28	699	301	699	102 5		
29			724	101 8	102 2	693
31	784	216	677	91 5		
32			684	93 7	92 6	697
33	815	185	554	80 0		
34			605	79 8		
35			596	81 4	80 4	654
36	839	161	532	76 8		
37			526	77 0	76 9	678
38	916	084	201	42 1		
39			198	49 7		
40			203	46 1	46 0	653
					Av k_1	689

$s = k_1[CO]^2[O_2]$, the curve so obtained is marked by the open circles in Fig. 3. This curve is seen to agree closely with the observed results.

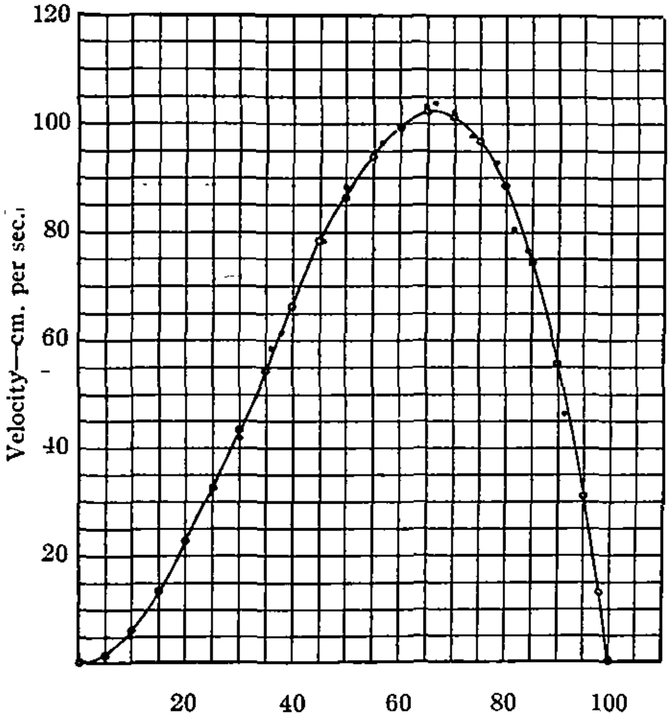

Fig. 3.—● Velocity observed. ○ Velocity = $k_1C^2_{CO}C_{O_2}$.

Remarks

A kinetic relation between the linear rate of movement of the zone in which the explosive reaction occurs and the concentrations of the active gases in which the zone is propagated, may prove indirectly of some value in the study of the rate of molecular transformation taking place within the flame, especially if the dimensions of the flame area, which appear to be sharply marked, could be determined with some accuracy during a reaction. Fundamentally, however, the method that has been described and the results given refer to the thermodynamics rather than to the kinetics of the reaction. The value of s is the linear rate at which an equilibrium condition is established. The method is concerned only with the initial and end conditions of an energy transformation as measured by gaseous volumes at constant pressure. The method takes no account of the way, usually complex, by which the reaction proceeds within the flame area. This fact may be shown by results already given. Fig. 3 shows the agreement between the observed value of s and a distribution curve for a tri-molecular reaction, $2CO + O_2 = 2CO_2$; yet this reaction is dependent upon intermediate reactions probably of the form[17] $CO + H_2O = CO_2 + H_2$ and $2H_2 + O_2 = 2H_2O$, so that the rate at which the reaction between carbon monoxide and oxygen completes itself must depend upon the rate at which the partial pressure of the water vapor present is maintained by the intermediate reaction.

If the partial pressure of the water vapor with which the explosive gases were saturated at their initial condition be gradually reduced while other conditions remain unchanged,[18] it will be found that the rate of flame propagation will be reduced also until a point is reached where the explosive reaction can not be induced in the gases; yet throughout these changes it will be found that s remains proportional to the product of the initial concentration, $[CO]^2[O_2]$. The value of the proportionality factor k_1 decreases rapidly with a decrease in the partial pressure of the water vapor present. The upper curve of Fig. 4 gives the observed values of s for this reaction at initial atmospheric conditions and water-vapor saturation. The lower curve shows the values for s for the same conditions except that the gases

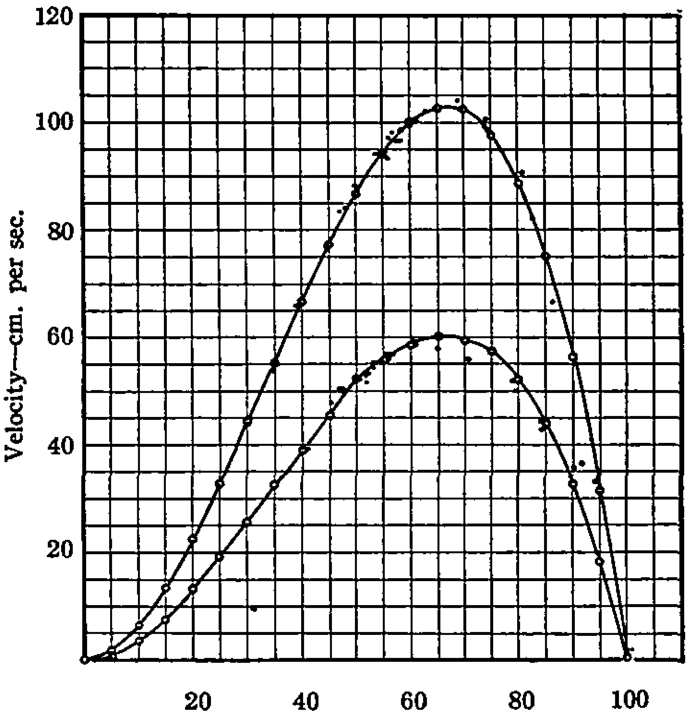

Fig. 4.—The effect of reduced water-vapor pressure on rate of flame movement.

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[17] Nernst, "Theoretical Chemistry," Macmillan, 10th edition, 1923, p. 791.

[18] The Bunsen-Gouy method (Refs. 3, 4, 5) employing a burner was made use of in these experiments, instead of the bubble.

are partially dried by chemical means. The value of k_1 for the upper curve is 692; for the lower, 405. If the gases are further dried by refrigeration and again brought to atmospheric conditions of temperature and pressure they cannot be exploded by a spark, although they will burn if again brought in contact with the oxygen and water vapor of the air.

The constant pressure p at which the reaction runs its course under the conditions imposed by the method just described is not the initial static pressure p_0 of the gases; but is their static pressure plus the impact pressure due to the linear rate at which the sphere of reaction is expanding,

$$p = p_0 + \frac{\rho}{2} s'^2 \tag{9}$$

where ρ is the initial density of the mixture of active gases. For values of s' not too near the velocity of sound in the gases it will be seen that the value of $(\rho/2)s'^2$ is small and may be negligible. But for values of s' above that of sound, it becomes the more important factor, because, under these circumstances, as Hugoniot[19] has shown, the law of static adiabatic no longer applies—the pressure in the impact wave at the seat of reaction increases for velocities above that of sound much more rapidly than the square of s'. It is, therefore, the pressure at the seat of reaction and not that indicated at a point more or less remote that should be considered in determining the pressure condition of the reaction and its effect upon reaction rate.

Applying the law of Hugoniot instead of the simple impact expression given in Equation 9, Chapman,[20] Jouguet,[21] Crussard,[22] and Becker[23] have made extended analyses of the impact pressure conditions accompanying the flame when its velocity of propagation exceeds that of sound in the gases. These are conditions applying to the high rates of flame propagation met with in the Berthelot explosive wave,[24] sometimes referred to as detonation, where the reaction runs its course at a constant impact pressure of many atmospheres. The flame velocity under these conditions is found, as in the case of much lower constant pressures described in this paper, to be strictly constant and, for tubes above 10 mm. diameter, quite independent of a container. The maximum flame velocity of the carbon monoxide–oxygen explosive reaction as found by the method described in this paper is 104 cm. per second at a pressure of one atmosphere. The maximum explosive wave velocity was found by Berthelot to be 166,900 cm. per second. The constant impact pressure accompanying the flame at this velocity is, according to Jouguet, 15.5 atmospheres.

[19] Hugoniot, *J. l'école polytech. Paris*, cahiers 57, 58 (1887).

[20] Chapman, *Phil. Mag.*, **47**, 90 (1899).

[21] Jouguet, *J. Math.*, **1**, 347 (1905); **2**, 5 (1906).

[22] Crussard, *Bull. soc. ind. min., St. Etienne*, [4] **6**, 1 (1907).

[23] Becker, *Z. Physik*, **8**, 321 (1923).

[24] Berthelot and Vieille, *Bull. soc. chim.*, **40**, 2 (1883).

The writer desires to express his gratitude to the National Advisory Committee for Aeronautics not only for generous financial support but also for continued interest and encouragement during an investigation of explosive gaseous reactions of which this paper is a partial report.

Summary

A condition under which the explosive gaseous reaction may run its course at constant pressure, thereby eliminating a variable factor affecting the concentrations of the explosive gases the flame is entering, may be closely realized in practice by holding temporarily the gases within a soap film container and firing the bubble from the center. This device functions as a bomb of constant pressure and thus provides the complement to the bomb of constant volume in the relation $pv = nRT$. Being transparent, it permits an accurate photographic time-volume record of the reaction to be secured. This record gives the initial volume r^3 of the active components of known concentrations, and, at the instant the action is completed, it gives the volume r'^3 of the equilibrium products which is the volume corresponding to the reaction constant

$$K = \frac{[A]^{n_1}\,[B]^{n_2}\,[C]^{n_3}}{[A']^{n'_1}\,[B']^{n'_2}\,[C']^{n'_3}}$$

Because the concentrations of the explosive gases that the flame is entering remain constant under the condition of constant pressure, it is found that the flame velocity under these conditions also remains constant during the reaction and that its value, s, is proportional to the product of the initial concentration of the gases,

$$s = k_1[A]^{n_1}\,[B]^{n_2}\,[C]^{n_3}$$

WASHINGTON, D. C.

[CONTRIBUTION FROM THE BUREAU OF METALLURGICAL RESEARCH, CARNEGIE INSTITUTE OF TECHNOLOGY]

THE CRYSTAL STRUCTURE OF MAGNESIUM PLUMBIDE

BY JAMES B. FRIAUF

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Magnesium is known to form intermetallic compounds with at least three elements in the fourth group of the periodic table, silicon,[1] tin[2] and lead.[3,2a] The crystal structures of magnesium stannide, Mg_2Sn and of magnesium silicide, Mg_2Si, have been completely determined by Pauling[4] and by Owens and Preston[5] and that of magnesium plumbide, Mg_2Pb, has been

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[1] Vogel, *Z. anorg. Chem.*, **61**, 46 (1909). Lebeau and Bossuet, *Rev. métal.*, **6**, 273 (1909).

[2] (a) Kurnakow and Stepanow, *Z. anorg. Chem.*, **46**, 177 (1905). (b) Grube, *ibid.*, **46**, 76 (1905).

[3] Grube, *ibid.*, **44**, 117 (1905).

[4] Pauling, THIS JOURNAL, **45**, 2777 (1923).

[5] Owens and Preston, *Proc. Phys. Soc. London*, **36**, 341 (1924).

partially determined by Sacklowski[6] who states that magnesium stannide and plumbide have face-centered cubic structures but does not specify the atomic arrangement in more detail. This paper confirms Sacklowski's results on the size and shape of the unit cell of magnesium plumbide and completes the determination of its structure by giving the way in which the atoms are arranged in the unit cell.

Magnesium plumbide was prepared by melting together the calculated amounts of magnesium and lead under a molten mixture of sodium and potassium chlorides to prevent oxidation. Since the compound is readily attacked by air, it was ground to a powder under kerosene, transferred to a piece of paper and covered with a thin coat of paraffin which effectually protected it from the action of the air. The flat sample was mounted on an X-ray spectrograph where it was rotated during the exposure and the powder diffraction pattern was photographed on a plate. Unfiltered radiation from a molybdenum target was used.

The observed values for the interplanar distances for all the planes producing reflections on the plate are shown in the second column of Table I and have the ratios required by a cubic crystal, the indices of the planes being those given in the first column. The third column of the table shows the values for a_0, the side of the unit cube, computed from the interplanar distances and the indices of the planes, and the last two columns show the

TABLE I

DATA

Plane	Interplanar distance	a	Intensity Obs.	Intensity Calcd
111β	3.926	6.800	5.5	6.5
111α	3.915	6.781	16.0	19.5
200α	3.390	6.779	5.4	5.2
220β	2.400	6.788	5.4	5.1
220α	2.400	6.788	13.5	15.3
113β	2.038	6.760	4.5	4.2
113α	2.043	6.772	12.0	12.5
222α	1.956	6.776	2.0	1.9
400β	1.692	6.770	1.4	1.1
331β	1.551	6.760	3.0	2.2
400α	1.698	6.791	3.9	3.4
331α	1.555	6.780	7.0	6.6
240α	1.518	6.789	3.5	3.1
333, 511β	1.300	6.756	2.9	2.0
224α	1.384	6.782	5.8	8.4
333, 511α	1.307	6.792	4.0	5.9
440α	1.203	6.808	2.1	3.0
351α	1.149	6.796	2.9	6.4
600α	1.130	6.777	Faint	0.4
620α	1.073	6.789	1.8	4.6
		Mean 6.78		

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[6] Sacklowski, *Ann. Physik*, 77, 241 (1925).

observed and computed intensities. The observed intensities are visual estimates made by comparison with a plate which had been given a series of known exposures. The mean value for a_0 is 6.78 Å. which is in good agreement with the value, 6.76 Å., given by Sacklowski.[6] With a_0 = 6.78 Å. and the density 5.5416,[3] the computed number of molecules in the unit cell is 4.09, or 4 within the limits of error.

The presence of only such reflections as have all indices odd, or all even, definitely eliminates the body-centered space-groups and strongly suggests that the only space groups which need to be considered are those based on a face-centered lattice. Reference to a tabulation of the results of the theory of space groups[7] shows that with this restriction there are three ways of arranging four lead and eight magnesium atoms in the unit cell, irrespective of any assumptions as to the equivalence of chemically like atoms. The intensities of the different lines were computed on the basis of each of these arrangements by the use of the customary intensity proportionality[8] $I\alpha(A^2 + B^2) \times j \times \left(\frac{d}{n}\right)^{2.35}$ where A and B have their usual significance as sine and cosine summations and j is the number of planes contributing to a single powder line. For two of the arrangements the computed intensity is greater for 200 than for 113 and as this conflicts with the data, these two arrangements are excluded. In the other arrangement the atoms have the following positions.

Pb at $0,0,0;\ \frac{1}{2},\frac{1}{2},0;\ \frac{1}{2},0,\frac{1}{2};\ 0,\frac{1}{2},\frac{1}{2}$
Mg at $\frac{1}{4},\frac{1}{4},\frac{1}{4};\ \frac{1}{4},\frac{3}{4},\frac{3}{4};\ \frac{3}{4},\frac{1}{4},\frac{3}{4};\ \frac{3}{4},\frac{3}{4},\frac{1}{4};\ \frac{3}{4},\frac{3}{4},\frac{3}{4};\ \frac{3}{4},\frac{1}{4},\frac{1}{4};\ \frac{1}{4},\frac{3}{4},\frac{1}{4};\ \frac{1}{4},\frac{1}{4},\frac{3}{4}$.

The intensities computed for this structure on the assumption of direct proportionality between scattering power and atomic number are shown in the last column of Table I and are in satisfactory agreement with the observed intensities. This is the simplest atomic arrangement that will account for the observed intensity relations in the powder diffraction pattern from magnesium plumbide and is known as the calcium fluoride arrangement. More complicated structures containing one or more variable parameters may be obtained from space groups based on a simple cubic lattice, but since these space groups should give odd order reflections from planes other than those with all indices odd except for values of the parameters which give them approximately the face-centered form, and since the calcium fluoride structure is in agreement with the data, there seems to be no necessity for resorting to these more general structures.

The positions of magnesium, silicon, tin and lead in the periodic table together with the fact that magnesium silicide, stannide and plumbide have

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[7] Wyckoff, "The Analytical Expression of the Results of the Theory of Space Groups," Carnegie Inst., Washington, 1922.

[8] Wyckoff, "The Structure of Crystals," Chemical Catalog Co., New York, 1924, p. 201.

the same kind of crystal structure as a typical polar compound, calcium fluoride, suggests that these three intermetallic compounds of magnesium are polar compounds.

Summary

The crystal structure of the intermetallic compound, magnesium plumbide, has been determined from X-ray diffraction data. The unit cell is cubic with an edge equal to 6.78 Å. and contains four molecules. The positions of the atoms are given by the calcium fluoride arrangement.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 185]

THE MOVING-BOUNDARY METHOD FOR DETERMINING TRANSFERENCE NUMBERS.[1] V. A CONSTANT CURRENT APPARATUS

BY DUNCAN A. MACINNES, IRVING A. COWPERTHWAITE AND KENNETH C. BLANCHARD

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In the determination of a transference number T from the motion of a single boundary the results are computed from the formula

$$T = VF/\phi it$$

V being the volume through which the boundary has swept, ϕ the volume containing a gram equivalent, F is the faraday, and i and t are, respectively, the current and time. It has not, in this work, been found convenient to obtain the product it with a coulometer, since the number of coulombs is too small to measure with accuracy. It has, therefore, been necessary, until our most recent work, to keep the current i constant by hand regulation. Since the solution whose transference numbers are to be measured is gradually replaced by indicator solutions which have lower conductances, the applied potential must be gradually increased if the current is to remain constant. This increase is accomplished by shifting the sliding contact of a rheostat shunting a portion of the storage cells used to supply the voltage. Hand regulation was found to be very tedious, and, especially, as readings of the position of the boundary must be made from time to time, not always accurate. We therefore decided to devise an apparatus for the automatic adjustment of the current. This apparatus has proved to be so satisfactory in operation that it should undoubtedly be useful in other connections.

The device finally adopted is shown in Fig. 1. Current is furnished to

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[1] The papers that have already appeared in this series are: I. MacInnes and Smith, THIS JOURNAL, **45**, 2246 (1923); II. Smith and MacInnes, *ibid.*, **46**, 1398 (1924); III. MacInnes and Brighton, *ibid.*, **47**, 994 (1925); IV. Smith and MacInnes, *ibid.*, **47**, 1009 (1925).

the moving-boundary apparatus M (which in all our later work has been of the type devised by MacInnes and Brighton) by the storage batteries A and B, the first yielding about 150 volts and the latter 100 volts. Battery B is shunted across the adjustable rheostat R of 1680 ohms. The potential across the terminals of the moving-boundary apparatus M can therefore be varied by shifting the contact point C. The current passing through the cell M is measured by determining the potential drop in the resistance R′, of 200 ohms, by means of the potentiometer P. The adjustment of this potentiometer is determined with the aid of the galvanometer G, the moving coil of which carries a pointer arm on which has been placed a light vane V of aluminum foil, the purpose of which will be made clear below.

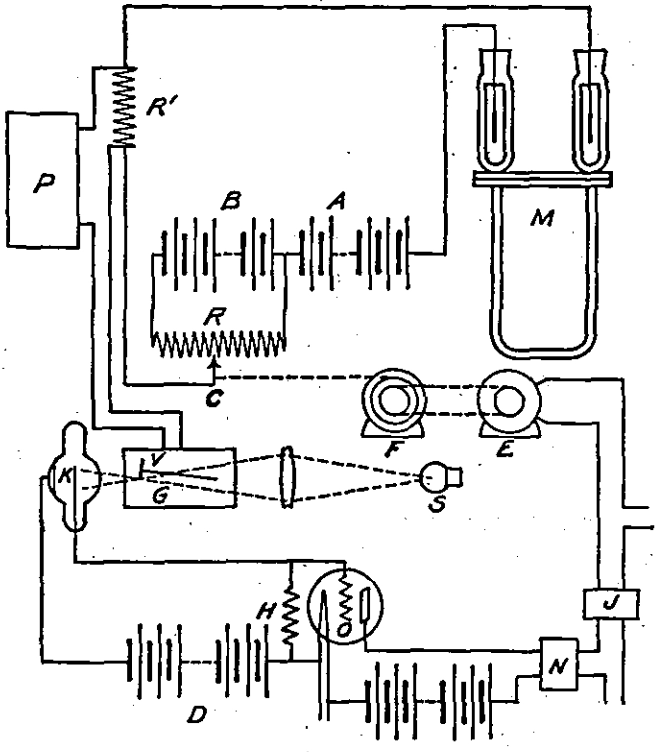

Fig. 1.

The contact point C of the rheostat R is moved mechanically by means of the electric motor E, which operates the reducing gears F. The motor is started and stopped by means of the following relay system. The line current (110 volts) passes through the ordinary relay J which is operated by the sensitive relay[2] N which in turn is actuated by the current, about one milliampere, that passes from the filament to the plate in the radio tube O. This current can be interrupted by placing a stopping potential on

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[2] Western Electric B 108 telephone relay.

the grid of the radio tube. This is accomplished by placing the photo-electric cell[3] K in series between the grid and the filament and the source of potential (about 100 volts) D. When the photo-electric cell is illuminated, sufficient current passes to keep the grid at a high enough potential to stop the current between the filament and the plate. An essential portion of the apparatus is the grid leak, H. Since it and the photo-electric cell K are in series with the potential D, the potential on the grid will depend on the relative resistances of the grid leak and the illuminated cell. A grid leak having a very large resistance (30 megohms) was thus found advisable. The illumination of the photo-electric cell is regulated by the motion of the vane V on the galvanometer G. An image of the filament of the light source S (a 21 c. p. headlight lamp) is focused sharply on the vane V by means of a lens, and a small motion (about 0.3 mm.) of the vane is sufficient to illuminate the cell or to darken it.[4] Thus a slight movement of the needle of the galvanometer is sufficient to stop and start the motor E. With our apparatus a difference of potential (between the drop in the resistance R′ and that furnished by the potentiometer) of 0.0003 volt is sufficient to actuate the relay system. Since the total potential drop in R′ is from 1.0 to 1.5 volts the regulation is from 0.03 to 0.02%. Accuracy of regulation is, however, limited by the lack of continuity of the adjustable resistance R which is of the usual sliding contact type with fine wires wrapped around a tube. Inaccuracies from this source are harder to estimate but they seem to be of the same order of magnitude as those just given.

TABLE I

TRANSFERENCE NUMBERS OF 0.1 *N* POTASSIUM NITRATE AT 25°

Indicator solutions: 0.068 *N* $LiNO_3$ and 0.072 *N* $KC_2H_3O_2$

Reading, cm.	Potassium ion			Nitrate ion		
	Volume, cc.	Seconds	Trans. no.	Volume, cc.	Seconds	Trans. no.
7	1.1247	3025	0.5123	0.9994	2825	0.4875
8	1.2831	3453	.5121	1.1416	3230	.4870
9	1.4423	3880	.5122	1.2821	3629	.4868
10	1.6016	4309	.5122	1.4207	4015	.4876

Probably the most effective method of showing the successful operation of this apparatus is to give the values from a typical determination of a transference number. The data obtained in such a determination are given in Table I. From these data the transference numbers of both ions of potassium nitrate have been computed from measurements made when the boundaries had moved through 7 to 10 cm. of the graduated tubes. By comparing the times in seconds (Cols. 3 and 6), with the corresponding

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[3] We have used the Kunz potassium photo-electric cell and one of the General Electric potassium hydride type and have found them equally satisfactory for this purpose.

[4] A galvanometer with a moving mirror was first used but a far more powerful light source was then found necessary.

transference numbers, it is evident that the movement of the boundary past a graduation mark must have been read, at least in the case of the positive ion, to the nearest second and, also, that the current must have been constant in this interval, within the range of error of the measurements, which was about 0.02%. The sum of the average values of the two transference numbers is 0.5122 + 0.4872 = 0.9994, or within 0.06% of unity. The only previously recorded value for a transference number of potassium nitrate (0.501 for the positive ion) is given by Denison and Steele;[5] this is evidently in error. A series of measurements on transference numbers of a series of nitrates, which present peculiarities which are interesting in the light of the modern theories of electrolytic dissociation, is now in progress.

The authors are indebted to the Warren Fund of the American Academy of Arts and Sciences for an appropriation which was of great assistance in this work.

Summary

An apparatus involving a photo-electric relay system is described. This device maintains a constant current, within 0.02–0.03%, through a moving-boundary apparatus, the resistance of which steadily increases during a determination. Data are given on the moving-boundary measurements on potassium nitrate solutions which indicate that regulation to that precision has been attained in practice.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF TUFTS COLLEGE]

THE VISCOSITIES OF SEVERAL AQUEOUS SOLUTIONS OF ORGANIC SUBSTANCES AND THE POLYMERIZATION OF WATER

BY HARRIS MARSHALL CHADWELL

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This investigation is a continuation of the study of aqueous solutions of non-polar materials from the point of view of the polymerization of water. In a recent paper[1] in collaboration with T. W. Richards it was shown that the changes in volume and in compressibility on solution of various organic materials could be explained adequately by consideration of (1) the cohesive affinities concerned, (2) the effect of polymerization of one or both liquids (and the possible formation of complex solvated molecules), and (3) the effect of the several compressibilities of the cohering substances. The present paper reports the determination of another property of the solutions and an attempt to explain the data by the same considerations.

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[5] Denison and Steele, *Trans. Roy. Soc. London.*, 205A, 449 (1906).

[1] Richards and Chadwell, THIS JOURNAL, 47, 2283 (1925).

The property of viscosity has been interpreted by many investigators[2] to reflect changes in molecular constitution, particularly the formation of complex molecules between the two components of the solution. The generally accepted explanation for the fact that aqueous solutions of such materials as the alcohols and acetic acid have a greater viscosity than water (even though the solute may have a smaller viscosity) is the formation of more or less definitely solvated molecules.[3] The existence of such definite hydrates would be more conclusive if the exact relationship between viscosity and concentration for an "ideal" solution[4] were known with certainty.

However, the property of viscosity should throw some light on the nature of the solutions previously studied. If water is depolymerized by the addition of a second substance, and the resulting water has a smaller viscosity (analogous to the effect of an increase in temperature) then the viscosity would tend to be less than for pure water. Such a result is found in dilute solutions of certain inorganic salts and has been called "negative viscosity."[5]

This paper records the viscosity determinations of solutions of methyl and ethyl acetates, ethyl ether and benzene in water, water in the esters, and methyl acetate in ethyl acetate.

The most striking outcome of the investigation is that aqueous solutions of organic materials seem to have a greater viscosity than pure water despite the fact that the pure solutes have a smaller viscosity.

Purification of Materials

Water.—Thrice distilled water (free from oil, organic matter, ammonia and carbon dioxide) was used.

Ethyl Acetate.—Commercial "anhydrous" ethyl acetate, neutral to litmus, was freed from alcohol after a preliminary drying with phosphorus pentoxide, by distilling with a trace of water according to the method of Wade and Merriman[6] using a 20-disk distilling head recommended by Young.[7] The ester was then dried by successive addi-

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[2] Reviewed in (a) Dunstan and Thole, "The Viscosity of Liquids," Longmans, Green and Co., London, **1914** (Monographs of Inorganic and Physical Chemistry, edited by Findlay); (b) Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., New York, **1922**; a very complete bibliography is included.

[3] Evidence of definite hydrate formation in aqueous solutions of H_2SO_4 and $FeCl_3$ from viscosity measurements is given by Smits, Lande and Bouman, *Proc. Acad. Sci. Amsterdam*, **23**, 969 (1921). For criticism and review, see Jorissen, *Rec. trav. chim.*, **40**, 281 (1921).

[4] (a) Kendall, This Journal, **36**, 1069 (1914). (b) Kendall and Brakeley, *ibid.*, **43**, 1826 (1921). (c) Kendall and Monroe, *ibid.*, **39**, 1787 (1917); (d) **43**, 115 (1921). (e) Kendall and Wright, *ibid.*, **42**, 1776 (1920). See also Ref. 2 b, p. 84 and following pages.

[5] Discussed very completely from this same point of view by Rabinovich, This Journal, **44**, 954 (1922).

[6] Wade and Merriman, *J. Chem. Soc.*, **101**, 2429 (1912).

[7] Young, *ibid.*, **75**, 679 (1899).

tions of phosphorus pentoxide over a period of six days, and finally fractionated from a Richards and Barry[8] flask and all-glass apparatus. In all distillations the greatest precautions were taken to protect the materials from moisture. All of the material distilled at the temperature of 77.15° (760 mm.), within the accuracy of reading the thermometer. All boiling points were measured with Anschütz thermometers graduated in 0.2° and standardized with an accuracy of ±0.05°. Portions of each of the three fractions had the same viscosity within the accuracy of measurement (0.05%). The density[9] ($d^{25}_{4\ \mathrm{vac.}}$) was 0.89451.

To confirm the belief that the ester was dry, about 250 ml. was shaken with approximately 35 g. of phosphorus pentoxide and the mixture allowed to stand for six hours. It formed a gel[10] rigid enough not to break when the flask was inverted. On being heated, the ester distilled at the same temperature and the distillate had the same viscosity as before.

Methyl Acetate.—Commercial "anhydrous" methyl acetate, neutral to litmus, and shown to be free from acetone by the salicyl aldehyde test,[11] was treated thrice with phosphorus pentoxide, as recommended by Young and Thomas[12] and then fractionated with the Young disk column. It was again treated with phosphorus pentoxide and distilled in the Richards flask, all of the material passing over at 57.2° (760 mm.) within 0.1°. Its purity was confirmed in the same way as was that of the ethyl acetate. Its density (d^{25}_4) was 0.92740, in good agreement with the determination of 0.92704 (interpolated) of Young and Thomas.[13]

Ethyl Ether.—One of the purest commercial preparations of "absolute" diethyl ether was treated with five successive portions of phosphorus pentoxide over a period of a week as recommended by Wade and Finnemore.[14] On fractionation in the Richards flask all of the material except the forerun distilled at 34.6°. Its density (d^{25}_4) was 0.70792, in good agreement with the determination of 0.70788 by Squibb.[15]

Benzene.—The benzene had been purified for molecular weight determinations by the method suggested by Richards and Shipley,[16] followed by six crystallizations.

Apparatus and Technique of Viscosity Determinations.—The measurements of viscosity were made with the modified Ostwald viscometer, developed by Washburn and Williams[17] but constructed of Pyrex glass instead of quartz. Although not adapted to such diversified uses as the viscometer of Bingham,[18] it can be used with greater ease for aqueous solutions.

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[8] Richards and Barry, THIS JOURNAL, 36, 1787 (1914).

[9] Others have obtained the following values (d^{25}_4): Kendall and Walden, 0.8938 [*Z. physik. Chem.*, **65**, 134 (1909)]; Hubbard, 0.89422 [*ibid.*, **74**, 217 (1910)]; Tyrer, 0.89450 [*J. Chem. Soc.*, **97**, 2624 (1910)]; Wade and Merriman, 0.89446 [*ibid.*, **101**, 2429 (1912)]; Willard and Smith, 0.8945 [THIS JOURNAL, **45**, 289 (1923)].

[10] Williams [THIS JOURNAL, **47**, 2649 (1925)] reports a similar gel with nitromethane, phosphorus pentoxide and a trace of water.

[11] Allen, "Commercial Organic Analysis," Blakiston, Philadelphia, **1912**, Vol. 1, p. 105.

[12] Young and Thomas, *J. Chem. Soc.*, **63**, 1191 (1893).

[13] Ref. 12, p. 1207.

[14] Wade and Finnemore, *J. Chem. Soc.*, **95**, 1842 (1909).

[15] Squibb, *Chem. News*, **51**, 66, 76 (1885).

[16] Richards and Shipley, THIS JOURNAL, **36**, 1825 (1914).

[17] Washburn and Williams, *ibid.*, **35**, 739 (1913).

[18] Described completely in Bingham, Ref. 2b, p. 295. Its use in a series of very careful investigations by Kendall and co-workers is there reported.

The instrument was modified slightly by blowing a bulb of about 0.2 ml. capacity at the top of the capillary, the lower of the two scratches being between this bulb and the higher reservoir. The constrictions beneath the scratches had a radius at least ten times that of the capillary according to the specifications of Bingham. The distance between the two scratches was 5.79 cm., the volume of liquid contained between them, 9.37 ml. The capillary was about 18.1 cm. in length, having a diameter of 0.0453 cm. In other details and dimensions the viscometer was essentially the same as that of Washburn and Williams. The three-way stopcock by which the arms of the viscometer could be connected together or opened to the atmosphere was found to be very convenient.

The viscometer was mounted in a brass frame of such construction that the capillary was held in the same vertical position when placed in the thermostat. This thermostat was of glass with a window in the heat-insulating material so that the viscometer could be seen easily. The temperature was maintained at 25.00° (±0.002°, corrected) by the usual automatic electric device.

The time of flow was measured by a stopwatch having an excellent Swiss movement of the sort that continued to run independently of the hands. It recorded the time to $^1/_5$ second. It was verified frequently by an horologist and during its use was kept at a constant state as regards winding and position.

The densities of the various materials were determined in 10-ml. Ostwald pycnometers and were calculated to the vacuum standard by the method proposed by Richards and Chadwell.[1] The density of water at 25° was taken as 0.99707.

The solutions of known composition by weight were prepared in glass-stoppered flasks of such size that very little gas space was left above the liquid. The more volatile constituent was added last. A constant volume (62 ml.) of liquid was transferred to the large bulb of the viscometer by means of a pipet, the pipet being filled quickly by the application of a pressure of dry, clean air on the liquid in the flask. By a similar method the small bulb was filled by forcing liquid from the larger bulb. After the viscometer and its contents had come to the temperature of the thermostat, and the stopcock had been opened momentarily to the atmospheric pressure, then turned to connect the two tubes of the viscometer, the time of flow was measured. After the time of flow had been taken, liquid was forced again into the smaller bulb by a pressure of clean, dry air and another run made. It would seem that this method of transferring liquid would change the concentration of the solution less than by applying suction to the other side of the viscometer. The time of flow as reported is a mean of several determinations, enough so that the time was certain within the accuracy of the stopwatch ($^1/_5$ sec.). There must have been a slight change in concentration of the solutions as the number of runs increased, but no trend in the times of flow was observed.

There must also have been a change in concentration due to the saturation of the air with the vapors from the solution. In the experiments with water solutions of ether and benzene, the viscometer was filled with air, previously dried and then bubbled through a large volume of a solution of the same concentration. This treatment would partially obviate the change in concentration due to evaporation.

After each run the viscometer was washed with chromic acid cleaning solution, dust-free water, alcohol and ether, and then dried with air previously passed through sulfuric acid and a long tube of absorbent cotton. Frequent runs were made with water to detect any change in the capillary or irregularity in technique. At no time did this time of flow vary from the mean result by more than the experimental error.

Calculation of the Results

The values of viscosity are calculated from Poiseuille's law with and without the application of the kinetic energy correction. Without the correction the relative viscosity is given by the well-known expression

$$\eta/\eta_0 = \frac{(d - D)\,t}{(d_0 - D)\,t_0} = \frac{\rho t}{\rho_0 t_0} \tag{1}$$

where the subscript zero refers to the data for water, d the density of the liquid in air, D the density of the air, ρ the density in vacuum and t the time.

When the vacuum correction is applied, the formula becomes, using the nomenclature of Bingham $\eta = Cpt - C'\rho/t$; $C = 384.8\ r^4/vl$; $C' = 0.0446\ v/l$, where η is the viscosity in poises, p is the "true average pressure" (g. per sq. cm.), r the radius (cm.) of the capillary, l its length (in cm.) and v the volume (ml.) of liquid. The constant in the expression for C is based on the value of 980 for the acceleration due to gravity. This expression can be modified to make it applicable to the Ostwald viscometer by substituting for Cp the term $K\rho$, the expression becoming

$$\eta = K\rho t - C'\rho/t \tag{2}$$

where K is a new constant and determined by a run with water, after C' has been calculated from the dimensions of the viscometer. This formula is slightly different from that used by Lewis,[19] in that the latter does not include the kinetic energy correction for water; and is also different from that suggested by Bingham and his collaborators[20] in which an attempt

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[19] Lewis, THIS JOURNAL, 47, 626 (1925).

[20] Bingham, Schlesinger and Coleman, *ibid.*, 38, 27 (1916). This paper reports the use of the Washburn and Williams viscometer without the application of any correction to the simple formula. The importance of the consideration of this pressure correction, when the Bingham viscometer is used, has been emphasized by Kendall and Monroe, *ibid.*, Ref. 4 c, p. 1787.

is made to correct for the "true average pressure." It is identical with the formula developed by Martin.[21]

In these calculations of viscosity no attempt has been made to correct for surface-tension effects.

The invariant factors used in the calculations are as follows: ρ_0 = 0.99707, t_1 = 706.6 sec., η_0 = 0.008949 poises,[22] K = 0.000012748, C' = 0.0231. The results are summarized by Table I, the data for solutions in water being shown in Fig. 1. In the first column are recorded the percentages by weight of the solute (the first substance given in the titles), in the second the time in seconds, in the third the densities in a vacuum, in the fourth the viscosity as calculated by Formula 1, in the fifth the viscosity as calculated by Formula 2. The viscosities are recorded in the table in units of millipoises (the values calculated from the above constants multiplied by 1000).

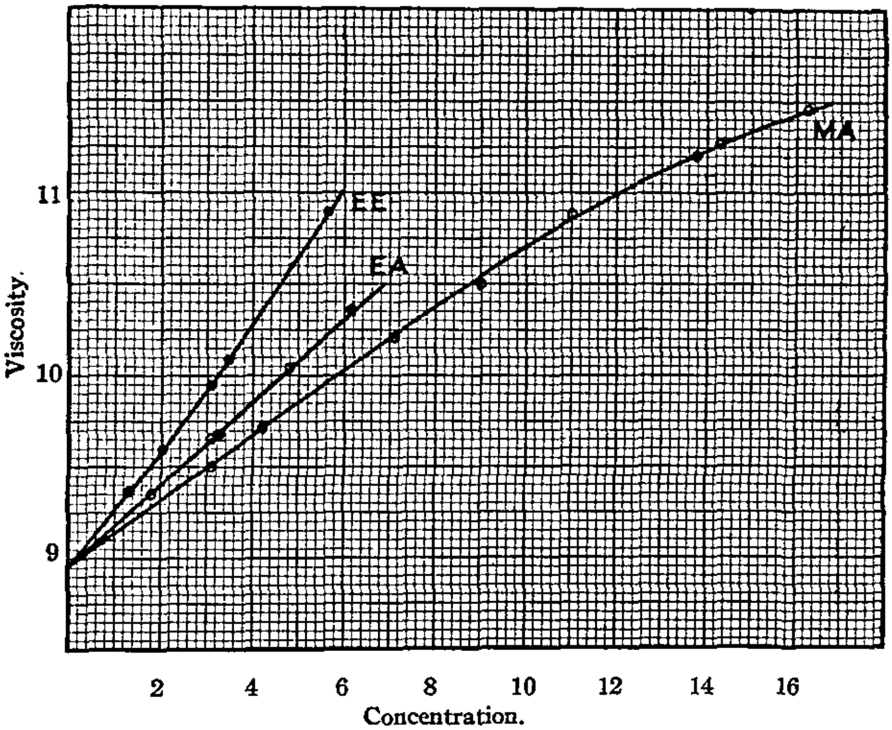

Fig. 1.—The change of viscosity of aqueous solutions at 25°; viscosity in millipoises are plotted as ordinates, and concentrations as weight percentages as abscissas.

Curve EE represents viscosities of aqueous solutions of diethyl ether, Curve EA represents viscosities of aqueous solutions of ethyl acetate, Curve MA represents viscosities of aqueous solutions of methyl acetate.

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[21] Martin, *Bull. soc. chim. Belg.*, **34**, 81 (1925).

[22] The value accepted by the International Critical Tables.

TABLE I

RESULTS OF VISCOSITY DETERMINATIONS AT 25°

	Time t sec.	Density (ρ) $\left(d^{25}_{4}\ \text{vac.}\right)$	Viscosity Millipoises η_I	η_{II}
Water	706 6	(0.99707)	(8.949)	(8.949)
Methyl acetate	309.8	.92740	3.649	3.594
Ethyl acetate	377.0	.89451	4.283	4.244
Ethyl ether	252.8	.70792	2.273	2.216
%	t	ρ	η_I	η_{II}
		ETHYL ACETATE IN METHYL ACETATE		
0.000	309.8	0.92740	3.649	3.594
9.159	314.6	.92399	3.692	3.638
21.698	322.4	.91962	3.766	3.713
36.562	331.5	.91456	3.851	3.801
48.840	339.3	.91045	3.924	3.876
59.560	346.3	.90695[a]	3.990	3.943
81.855	362.2	.90000[a]	4.140	4 098
89.295	368.4	.89774	4.201	4.158
100.000	377.0	.89451	4.283	4.244
		METHYL ACETATE IN WATER		
0.000	706.6	0.99707	8.949	8.949
3.122	749.6	.99792	9.501	9.505
4.215	765.5	.99824	9.706	9.711
7.113	803.5	.99901[a]	10.196	10.214
9.010	826.6	.99947	10.494	10.504
11.077	854.7	.99997[a]	10.856	10.869
13.793	878.8	1.00038	11.166	11.181
14.295	886.0	1.00045	11.260	11.274
16.259	900.3	1.00060	11.442	11.458
		WATER IN METHYL ACETATE		
0.000	309.8	0.92740	3.649	3.594
1.730	319.4	.93004	3.773	3.720
3.248	331.8	.93250	3.930	3.879
5.025	347.7	.93532[a]	4.131	4.084
6.671	365.4	.93823	4.354	4.311
		ETHYL ACETATE IN WATER		
0.000	706.6	0.99707	8.949	8.949
.676	718.1	.99704[a]	9.094	9.095
.892	720.8	.99702	9.128	9.129
1.815	738.4	.99698	9.351	9.354
3.041	761.8	.99692	9.646	9.652
3.284	763.8	.99690[a]	9.671	9.678
4.809	792.5	.99682	10.034	10.043
6.170	817.1	.99675	10.346	10.357
		WATER IN ETHYL ACETATE		
0.000	377.0	0.89451	4.283	4.244
.890	382.2	.89610	4.349	4.312
1.658	388.8	.89745[a]	4.432	4.395
2.459	396.8	.89891	4.530	4.495

Table I (*Concluded*)

%		ρ	η_I	η_{II}
		Ethyl Ether in Water		
0.000	706.6	0.99707	8.949	8.949
1.360	741.5	.99413	9.363	9.366
2.060	760.5	.99301[a]	9.592	9.597
3.089	790.2	.99164	9.953	9.959
3.485	801.5	.99106[a]	10.090	10.099
5.848	864.0	.98791	10.841	10.883

[a] Values were obtained by interpolation.

The viscosities of the pure materials may be compared with those obtained at this same temperature by other investigators. The result for ethyl acetate (4.244) is in very good agreement with the value of 4.239 reported by Kendall and Wright.[4c] Their result is calculated from the value of 8.946 for water. When changed to the same value for water (8.949) as used above, the result is 4.241. The value of 2.216 for ethyl ether is slightly lower than 2.233 found by Kendall and Wright and 2.231 by J. R. Lewis.[23]

It was found that the viscosity of water saturated with benzene differed appreciably from that of water. Two saturated solutions were prepared in the thermostat at 25°. They gave times of flow of 709.3 and 709.4 seconds, a density of 0.9968 and values of η of 8.981 and 8.982, respectively. The concentration of this saturated solution is not known exactly. As has been pointed out recently by A. E. Hill,[24] Hantzsch[25] gives the value of 0.113% by weight of benzene at 25°; Herz[26] 0.08% at 22°; Moore and Roaf[27] 0.15% at 15°; and Hill[24] 0.15% at 0°.[28]

Discussion of Results

According to the present conception of solutions[29] the system, methyl acetate-ethyl acetate, should be nearly ideal, and so it is of interest to ascertain which of the various formulas that have been proposed for ideal solutions represent these experimental results. The two most satisfactory formulas are those of Kendall[30] and of Bingham. They are, respectively: $\eta^{1/3} = x\eta_1^{1/3} + (1-x)\eta_2^{1/3}$; and $1/\eta = x/\eta_1 + (1-x)/\eta_2$,

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[23] Lewis, This Journal, 47, 626 (1925).

[24] Hill, *ibid.*, 45, 1155 (1923).

[25] Hantzsch, *Z. physik. Chem.*, 30, 295 (1899).

[26] Herz, *Berl. Ber.*, 31, 2669 (1898).

[27] Moore and Roaf, *Proc. Roy. Soc.*, 77B, 96 (1905).

[28] Arrhenius [*Z. physik. Chem.*, 1, 285 (1887)] reports the following data for relative viscosities at 24.7°: (% by vol.) methyl acetate: 5%, 1.092, 2%, 1.035; ethyl acetate: 5%, 1.114, 2%, 1.044; ether: 7.5%, 1.224, 5%, 1.146.

[29] Hildebrand, "Solubility," Chemical Catalog Co., New York, 1924, pp. 23, 86.

[30] Kendall and Wright, Ref. 4e, record the application of these formulas to systems of other esters.

where η is the viscosity of the solution, η_1 and η_2 are the viscosities of the pure materials and x is the mole fraction of the component whose viscosity is η_1. The comparison between calculated and experimental results is given in Table II.

TABLE II

COMPARISON OF CALCULATED AND EXPERIMENTAL VALUES OF VISCOSITIES OF SOLUTIONS OF METHYL AND ETHYL ACETATE

Viscosities expressed in millipoises at 25°

η Ethyl acetate = 4.244 η Methyl acetate = 3.594

% (by wt.) Et. Ac.	Mole fraction Et. Ac.	η calculated by equation of Kendall	Bingham	Observed η
9.16	0.0782	3.645	3.639	3.638
21.70	.1892	3.709	3.701	3.713
36.56	.3264	3.804	3.783	3.801
48.84	.4454	3.877	3.856	3.876
59.56	.5533	3.944	3.926	3.943
81.86	.7915	4.104	4 090	4.098
89.30	.8753	4.158	4.151	4.158

Average deviation from Kendall's formula = 0.003
Average deviation from Bingham's formula = 0.012

It would seem that Kendall's formula is more satisfactory than the second since it represents the viscosities within the experimental error—a deviation of 0.001 millipoise in viscosity corresponding to 0.15% in composition and 0.1 second of time. However, the viscosities of the pure substances are too nearly alike to afford a conclusive test for any formula. Bingham has shown that the rule of additive fluidities does not hold when there is a volume change, that the observed viscosity is greater than the calculated when there is a contraction. This does not explain the divergence of the rule above, for there is a slight expansion (never greater than 0.8 ml. per liter as in the case of the solution containing 48.8% ethyl acetate), and the observed values are consistently higher than the calculated. It seems that Kendall and Wright[31] are correct in stating that the perfect solution equation has not yet been satisfactorily developed and must await the advent of an adequately developed theory of liquids.

The results for the solutions containing water are the most interesting. They show very conclusively that the decrease in viscosity resulting from a depolymerization of water[32] is more than balanced, at least at this temperature, by one or more tendencies that cause an increase. It is to be remembered that changes in polymerization were reflected in the properties of density and compressibility. The viscosity would be decreased by the breaking up of bulky polymerized solvent molecules. All of the solutes used possess viscosities very much lower than that of water.

[31] Ref. 4 e, p. 1783.

[32] See, for example, Röntgen, *Wied. Ann.*, 52, 510 (1884). Sutherland, *Phil. Mag.*, [V] 50, 460 (1901). Richards and Palitzsch, THIS JOURNAL, 41, 59 (1919).

The data confirm a generalization pointed out long ago by Arrhenius[33] but not emphasized recently, that aqueous solutions in general have a viscosity greater than that of water, even though the viscosity of the solute may be very low. Practically all aqueous solutions of organic materials possess a greater viscosity than water, for example,[34] the alcohols, the acids, acetone, and various amines. To this list may now be added with assurance two esters, an ether and a hydrocarbon. The only materials so far investigated at this temperature which produce aqueous solutions of lower viscosity seem to be those inorganic salts showing "negative viscosity." This latter phenomenon has been adequately explained[35] by the theory of the dissociation

TABLE III

CONTRACTION AND SMOOTHED VALUES OF VISCOSITY

Solute %	Concentration, moles per liter	Contraction, ml. per liter	Increase in η_{II} (mp.)
	METHYL ACETATE IN WATER		
1	0.14	1.1	0.180
2	.27	2.1	.360
3	.40	3.2	.540
4	.54	4.2	.720
5	.68	5.2	.895
6	.81	6.1	1.074
10	1.35	10.2	1.750
15	2.01	14.8	2.385
	ETHYL ACETATE IN WATER		
1	0.11	1.1	0.218
2	.23	2.2	.446
3	.34	3.3	.678
4	.45	4.3	.908
5	.57	5.4	1.140
6	.68	6.5	1.368
	ETHYL ETHER IN WATER		
1	0.14	1.9	0.305
2	.27	4.1	.630
3	.40	6.8	.969
4	.53	9.3	1.312
5	.67	12.0	1.650
6[a]	.80	14.8	1.992

	WATER IN METHYL ACETATE						WATER IN ETHYL ACETATE		
Solute, %	1	2	3	4	5	6	1	2	3
Contraction, ml. per l.	1.1	2.2	3.3	4.4	5.5	6.6	1.0	2.3	4.3
Increase in η_{II} (mp.)	0.066	0.152	0.258	0.372	0.495	0.624	0.079	0.182	0.309

[a] Extrapolated.

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[33] Arrhenius, *Z. physik. Chem.*, **1**, 285 (1887).

[34] For many cases, see Landolt-Börnstein-Roth-Scheel, "Tabellen," 5th Ed., 1923, Vol. 1, p. 137 and following pages.

[35] Rabinovich, Ref. 5.

of polymerized water. At lower temperatures, urea[36] composed of relatively small molecules produces aqueous solutions of smaller viscosity than water.

The commonly accepted explanation[37] for such data showing increasing viscosity, and possibly a maximum, is the formation of solvated molecules. Such hydrates very probably exist in many cases,[38] but the general occurrence of increased viscosity, as pointed out above, with such a diversification of solutes possessing very different affinities for water suggests the search for other explanations.[39]

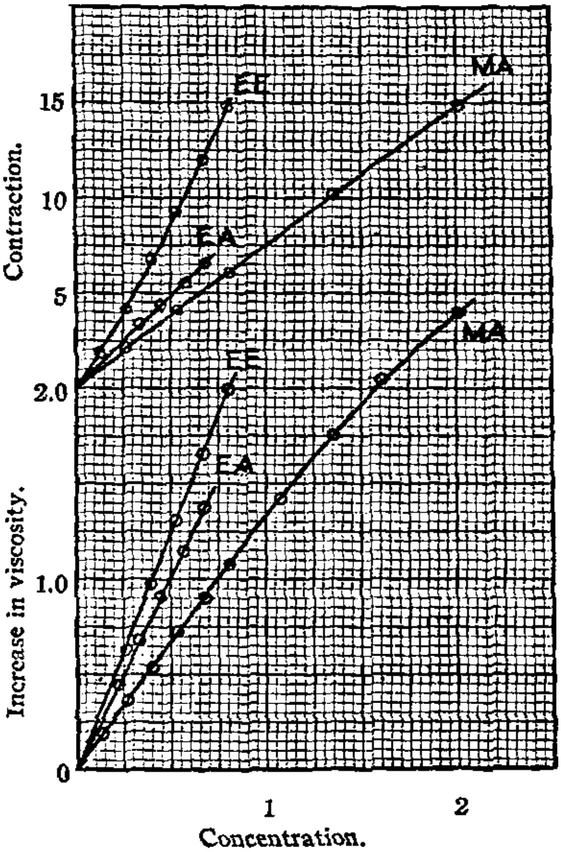

Fig. 2.—The parallelism between increase of viscosity and contraction of aqueous solutions at 25°. The increases of viscosity in millipoises and contractions in ml. per liter are plotted as ordinates and the molal concentrations per liter as abscissas.

Curve EE refers to aqueous solutions of diethyl ether, EA to aqueous solutions of ethyl acetate and MA to aqueous solutions of methyl acetate.

That there is often a close connection between contraction in volume and increase in viscosity has been emphasized by many investigators (reviewed by Bingham). The increase in viscosity of these particular solutions is also accompanied by a contraction, as shown in Table III. In the first column is given the concentration of solute expressed as per cent. by weight; in the second, as moles per liter of solution; the third gives the contraction in milliliters resulting in the formation of one liter of solution, and the fourth gives the difference in viscosity between the solution and solvent, expressed as millipoises.

The data for aqueous solutions given above are depicted in Fig. 2, where contraction and increase in viscosity are plotted as ordinates and concentrations as moles per liter as abscissas. The close similarity between the change in these two proper-

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[36] Mützel, through Bingham, Ref. 2 b, p. 179.

[37] Dunstan and Thole, *J. Chem. Soc.*, **95**, 1556 (1909). Thole, Mussell and Dunstan, *ibid.*, **103**, 1108 (1913).

[38] See, for example, Scatchard, This Journal, **43**, 2406 (1921).

[39] See Frank, *Z. physik. Chem.*, **114**, 257 (1924).

ties is very evident and perhaps this volume change may be the chief explanation for the change in viscosity. MacLeod,[40] for instance, has suggested that both the contraction and the increase in viscosity are due to a decrease in "free space" in the liquids.

It has been suggested by Tammann[41] that the materials in solution behave as if they were under pressure. The magnitude of the change in viscosity given above is in the same order as the change in viscosity of the various solutes caused by external pressure. Bridgman[42] has shown recently that for pure liquids the volume and viscosity changes are not parallel, that with an increase in pressure the viscosity increases the most with substances having complex molecules. With a change of a given external pressure (2000 kg./sq. cm.) the viscosity of ether is greater than that of ethyl acetate, which in turn is greater than that of methyl acetate (Bridg-

Table IV

The Relative Viscosities of Aqueous Solutions of 5% (by Weight) of Non-Electrolytes Compared to the Molecular Volumes of the Solute at 25°

Substance	Relative viscosity (water = 1)	Molecular volume	Absolute viscosity (mp) (water = 8 95)
Urea[a]	1.05	45.4	
Acetone[b]	1.07	73.9	3 46
Methyl acetate	1.100	79.8	3.65
Urethan[c]	1.13 (20°)	82.1	
Pyridine[d]	1.12	91.1	8 8
Ethyl acetate	1.128	98.6	4.28
Benzene	(1.16)	89.6	6 05
Ethyl ether	1.185	104.7	2.27
Methyl alcohol[e]	1.138	40.7	5.53
Ethyl alcohol[e]	1 254	58.5	11.15 (99.2%)
n-Propyl alcohol[e]	1.260	75.0	19.36
Acetic acid[e]	1.098	57.4	12.23 (99.1%)
Nicotine[f]	1.544 (20°)	161.0	45.36

[a] Mützel, through Bingham, Ref. 2 b, p. 181.

[b] Jones and collaborators, *Carnegie Inst. Pub.*, **180**, 119 (1913).

[c] Richards and Palitzsch, This Journal, **41**, 59 (1919).

[d] Faust, *Z. physik. Chem.*, **79**, 97 (1912).

[e] Ref. 37.

[f] Tsakalotos, *Bull. soc. chim.*, **5**, 397 (1909).

The relative viscosities are interpolated, assuming linearity from zero concentration to the first reported determination. The viscosity for the benzene solution is an extrapolated value, assuming that the saturated solution had a concentration of 0.113%. The densities used in calculating molecular volume are those reported by the several investigators.

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[40] MacLeod, *Preprints Faraday Soc.*, **1923, 1925**; *Trans. Faraday Soc*, **20**, 348 (1924); through *C. A.*, **17**, 2211; **19**, 1361, 2152.

[41] Tammann, "Über die Beziehungen zwischen der inneren Kräften und Eigenschaften der Lösungen," Leopold Voss, Hamburg and Leipzig, **1907**.

[42] Bridgman, *Proc. Nat. Acad. Sci.*, **11**, 603 (1925).

man does not record data for methyl acetate but the relative magnitude is evident from his table and conclusions).

Another very important consideration in determining the viscosity of an aqueous solution of a non-electrolyte seems to be the molecular volume of the solute.[43] This is confirmed by Table IV in which is shown the relative viscosity (water = 1) of aqueous solutions having the arbitrarily chosen concentration of 5% by weight.[44]

This table seems to show that when the solute is normal[45] the larger the molecular volume, the larger is the relative viscosity, the viscosity of the pure solute playing a less important role. As would be expected, the alcohols and acetic acid do not behave normally.

That the bulky solute molecules contribute to an increase in viscosity is only logical, for the internal pressures[46] under which the solutes exist in the water are probably approximately the same, and the viscosity is then influenced by the bulk (and possibly the shape) of the particles. The viscosities of the pure liquids, on the other hand, are less significant because the internal pressures and cohesive forces are different in the different liquids. As a consequence it is logical to suppose that the properties of the molecules would be different in a solution than when these molecules exist under the influence of similar molecules in the pure liquid. This effect of the volume of the solute molecules is probably one of the most important of the tendencies which overbalance the effect of the depolymerization of the water.

I wish to express my indebtedness and gratitude to the Elizabeth Thompson Science Fund for providing mechanical aid in the calculations.

Summary

This paper gives results of viscosity determinations at 25° with a Washburn and Williams viscometer of the following solutions: methyl acetate in ethyl acetate, methyl acetate in water, water in methyl acetate, ethyl acetate in water, water in ethyl acetate, ethyl ether in water, and a saturated water solution of benzene. The densities are also recorded.

The general phenomenon is emphasized that aqueous solutions of nonpolar material possess a greater viscosity than water even though the solute possesses a smaller viscosity.

The parallelism between contraction on solution and increase in viscosity (with these particular substances) is indicated.

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[43] Very kindly suggested by Professor T. W. Richards.

[44] If the ideal solution equation were known with certainty, it would be more illuminating to compare the divergence of various aqueous solutions containing the same molal concentration, with the molecular volume of the solute.

[45] See Turner, "Molecular Association," Longmans, Green and Co., London, 1915, p. 164.

[46] For a review and bibliography, see Richards, *Chem. Rev.*, **2**, 315 (1925).

The data are discussed from the point of view of the polymerization of water and the internal pressures concerned.

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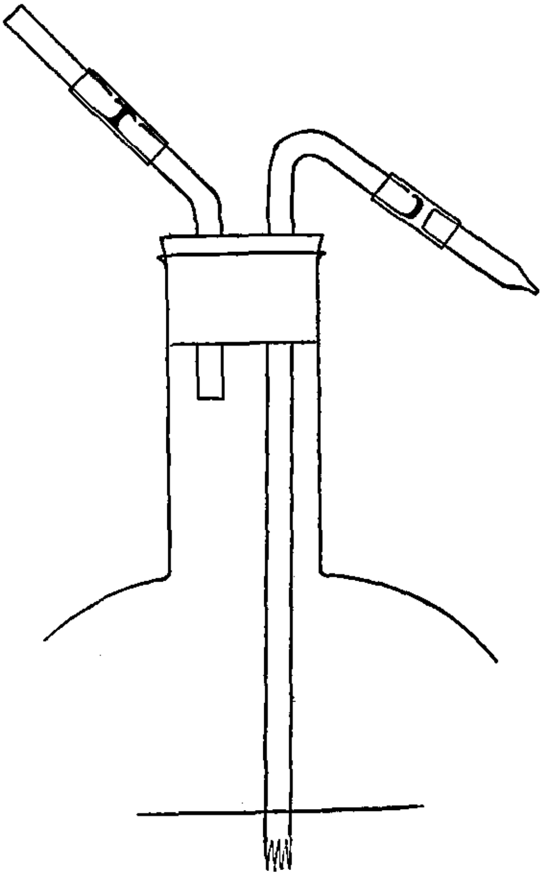
NOTE



A Non-Spattering, Continuous-Stream Wash Bottle.—The equivalent of two Bunsen valves serves to combine in one bottle in a way which is apparently novel two useful features, to wit—

First, the tip is kept full at all times, preventing spattering.

Second, it is not necessary to blow while using the bottle, as one breath expels 50 to 75 cc. of water.

Short sections of rubber tubing slipped over the glass tubes act as valves, a slight lateral pressure serving to open them. A liter flask about one-third full provides sufficient air capacity. If warm water is desired, the bottle may be kept on a warming oven. It is then unnecessary to provide for blowing as the combined pressure of air and water vapor suffices.

This bottle was designed and used at Northwestern University in 1924.

Berkeley, California
Contribution from the
University of California and
Yale University

H. E. Bent
G. A. Hunt

Received December 5, 1925
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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF IOWA STATE COLLEGE]

THE FORMATION OF ETHYL MERCAPTAN FROM ETHYL IODIDE IN AQUEOUS HYDROGEN SULFIDE SOLUTIONS AND ITS BEARING ON THE MECHANISM OF THE PRECIPITATION OF METALS BY HYDROGEN SULFIDE

BY F. E. BROWN AND J. E. SNYDER

RECEIVED AUGUST 11, 1925 PUBLISHED JULY 6, 1926

A recent paper on "The Mechanism of the Precipitation of Metals by Hydrogen Sulfide"[1] closes with the statement, "After a careful consideration of the evidence including that offered in the experimental part, the writers do not hesitate to draw the conclusion. . . .that the precipitation of the heavy metals with hydrogen sulfide, both in acid and in alkaline solutions, will eventually be regarded in the light of the coördination theory of Werner, as are already so many of the subjects of chemistry."

The evidence presented includes several lines of experiment and citation. Among others Smith and Semon describe the following experiments.

> "Into each of six numbered test-tubes, almost filled with freshly saturated hydrogen sulfide water, about 1 cc. of ethyl iodide or bromide was introduced. Nothing further was added to Mixture No. 1; to Nos. 2, 3 and 4, respectively, freshly precipitated ferrous sulfide, cadmium sulfide and mercuric sulfide were added; to No. 5 was added a slightly acidified solution of ferrous chloride; and to No. 6, dried and heated mercuric sulfide, either black or red. The tubes were then tightly stoppered and allowed to stand. In Nos. 2, 3 and 4, the odor of mercaptan was detected within two or three hours, and in No. 4, in case ethyl iodide was used, crystals of mercuric iodide appeared within a week. In No. 6, the odor of mercaptan was noted in about a week; but in Mixtures 1 and 5 the odor of mercaptan could not be detected at any time during a month."

From this group of experiments the following conclusions were drawn.

> "The formation of mercaptan as noted in these experiments cannot be ascribed to a direct reaction between hydrogen sulfide and ethyl halide, because, in the absence of metallic sulfide, these substances yield no mercaptan. Nor can the formation of the mercaptan be ascribed to a catalytic action of the metallic ion because, in the absence of metallic sulfide, no mercaptan is formed in the mixture containing ferrous chloride. We are forced to the conclusion that in the tubes containing the sulfide precipitates, in which alone mercaptan formation takes place, *both hydrosulfide and sulfide are present, in equilibrium, and that the formation of mercaptan is due to an exchange of halogen for hydrosulfide radical.* The formation of the mercaptan may therefore be represented by the following equations: $MS + H_2S \rightleftharpoons M(SH)_2$; and $M(SH)_2 + 2C_2H_5I \rightleftharpoons MI_2 + 2C_2H_5SH$."

As small an amount of ethyl mercaptan as 2×10^{-9} mg. is said to be detectable by odor.[2] If mercaptan forms by the reaction between ethyl iodide and precipitated sulfides, it might form from ethyl iodide and a saturated solution of hydrogen sulfide in which the concentration of SH ions[3] is 0.95×10^{-4} at 25°.

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[1] Smith and Semon, THIS JOURNAL, 46, 1325 (1924).

[2] Norris, "Organic Chemistry," second ed., McGraw-Hill Book Co., 1922, p. 362.

[3] Stieglitz, "Qualitative Chemical Analysis," The Century Co., 1921, Vol. I, Part II, p. 200.

If this concentration is insufficient, however, there should be an HS-ion concentration obtainable by adding ammonium hydroxide to the hydrogen sulfide solution which would be sufficient to form mercaptan. The concentration of the hydrogen ion should be more important than the presence of precipitated sulfides unless adsorption plays an important part in the reaction. The effect of concentration of hydrogen ion on the formation of mercaptan from ethyl iodide in a saturated solution of hydrogen sulfide was determined by varying the acidity of the solution.

Experimental Part

Effect of Acidity on Formation of Mercaptan.—Five cc. of freshly saturated hydrogen sulfide water was placed in each of twenty numbered test-tubes. No acid or base was added to No. 1; to Nos. 2 to 10 were added increasing amounts of ammonium hydroxide; and to Nos. 11 to 20 were added increasing amounts of hydrochloric acid.

The acidity ranged from 3 *N* acid through neutral to 3 *N* base. Five drops of ethyl iodide were then added to each. The tubes were stoppered and allowed to stand for one day Upon opening the tubes, the odor of mercaptan was detectable in every tube, the intensity decreasing with the acidity. Contrary to Smith and Semon's results,[1] these experiments show that mercaptan *is* formed by the action of ethyl iodide on hydrogen sulfide in the absence of precipitated sulfide, and even in acid solutions.

Effect of Sulfides on Formation of Mercaptan in Hydrogen Sulfide Water.—Hydrogen sulfide alone, lead, antimonous, mercuric, silver, cupric, bismuth, cadmium and stannic sulfides were used in this experiment. Each metal sulfide was freshly precipitated, washed with distilled water, and then transferred to a test-tube containing freshly saturated hydrogen sulfide water. After the mixture had been shaken for an hour, 5 cc. was transferred to another tube. To the remainder, neutral salt was added if necessary to coagulate colloidal material, and the mixture was filtered. Five cc. of the clear filtrate was then transferred to another tube. A tube containing 5 cc. of hydrogen sulfide water alone was also prepared. Into each of the tubes thus prepared, five drops of ethyl iodide were introduced. The tubes were stoppered and allowed to stand. At intervals of 15 minutes each tube was opened, and the time noted until the first odor of mercaptan was detectable. The results are given in Table I.

TABLE I

SULFIDES IN HYDROGEN SULFIDE WATER

Sulfide	H_2S and all filtrates	PbS	Sb_2S_3	HgS	AgS	CuS	Bi_2S_3	CdS	SnS_2
Time in hrs. and min. before C_2H_5SH is detected	12	2:15	2:15	2	2:30	2:30	2:15	2	2 15

These results show that precipitated sulfides greatly accelerate the formation of mercaptan in hydrogen sulfide solutions. This may, however, be due in whole or in part to the adsorption of hydrogen sulfide and ethyl iodide by the precipitated sulfides.

To determine whether other adsorbents have an accelerating effect similar to that of the precipitated sulfides, the following experiments were made.

Effect of Adsorbing Agents on the Formation of Mercaptan in Hydrogen Sulfide Water.—The adsorbing agents used in this experiment were bone black, charcoal, aluminum hydroxide, gelatin, barium sulfate, cotton, potato starch and silicic acid.

Each of the above substances containing no added metal sulfide was washed and placed in a test-tube containing 5 cc. of freshly saturated hydrogen sulfide water. Five drops of ethyl iodide were added to each. The tubes were stoppered and the time elapsing before the formation of mercaptan was determined as before. The results are given in Table II.

TABLE II

ADSORBING AGENTS IN HYDROGEN SULFIDE WATER

Substance	H_2S alone	Bone black	Charcoal	$Al(OH)_3$	Gelatin	$BaSO_4$	Cotton	Potato starch	Silicic acid
Time in hrs. and min. before C_2H_5SH is detected	12	1:45	12	1	6	3	10	8	12

These results show that some adsorbing agents greatly accelerate the formation of mercaptan. It is quite conceivable that the metal sulfides act in a similar manner.

Conclusions

1. The formation of ethyl mercaptan from ethyl iodide and hydrogen sulfide in the absence of solids and the retarding effect of the increase in the concentration of hydrogen ions indicate that the HS-ion is one of the reactants.

2. The fact that adsorbing agents other than freshly precipitated metal sulfides also increase the rate of reaction between ethyl iodide and hydrogen sulfide would indicate that adsorption instead of the formation of complexes of the Werner type causes the increase in rate of formation of ethyl mercaptan, when these solids are present.

Summary

1. Ethyl mercaptan forms when ethyl iodide is introduced into aqueous solutions of hydrogen sulfide. The rate of its formation decreases as the acidity increases.

2. The presence of freshly precipitated metal sulfides or of some adsorbing agents increases the rate of formation of ethyl mercaptan from ethyl iodide in saturated hydrogen sulfide solutions.

AMES, IOWA

[CONTRIBUTION FROM KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

A METHOD FOR DETERMINING SMALL QUANTITIES OF WATER IN METHYL ALCOHOL[1]

BY MARY M. RISING AND JOSEPH S. HICKS

RECEIVED OCTOBER 17, 1925 PUBLISHED JULY 6, 1926

The need has been felt for some time by research workers in this Laboratory for a short but accurate method of detecting traces of water in methyl alcohol and of measuring the amount of water present. Such a method could be used conveniently to follow the progress of dehydration of ordinary methyl alcohol by successive treatments with a suitable drying agent. The method would be of use further to demonstrate at any time the presence or absence of water in methyl alcohol which has been previously dried and set aside for future use.

Accordingly, the authors have investigated the effect of small quantities of water upon methyl alcohol dissolved in a solvent chosen to fit the necessities of the case. Crismer,[2] Alexejew,[3] Rothmund[4] and Timmermans[5] have worked extensively upon the mutual solubility of two liquids, and the effect of a third component upon such a system. Crismer studied the behavior of alcohols in ligroin, and the effect of the addition of traces of water to such mixtures, and was the first to make use of the consequent change in physical properties of the mixtures as a test for the purity of alcohols.

Methyl alcohol may be completely dissolved in a chosen solvent, say, at room temperature. When the temperature of the clear solution is lowered beyond the point of complete miscibility a second phase appears. When the mixture is warmed again, at a definite temperature, which may be designated as the solution temperature, the second phase disappears and all parts of the solution are again *identical in composition. The solution* temperature depends upon the relative concentrations of the two components. Further, the solution temperature is changed by the introduction of a third component, water, and the amount of change is fixed for a definite amount of water. That is, there is a fixed solution temperature for definite concentrations of the three components of the mixture alcohol, solvent and water.

We therefore undertook to determine solution temperatures for methyl

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[1] This paper describes work done by Joseph S. Hicks in partial fulfilment of the requirement for the degrees of Master of Science and Doctor of Philosophy at the University of Chicago, **1925**.

[2] Crismer, *Bull. acad. roy. Belg.*, [3] **30**, 97 (1895); *Bull. soc. chim. Belg.*, **18**, 18 (1904); **20**, 294 (1906).

[3] Alexejew, *Wied. Ann.*, **28**, 305 (1886).

[4] Rothmund, *Z. physik. Chem.*, **26**, 433, 455 (1898). "Löslichkeit und Löslichkeitbeeinflussung," Barth, Leipzig, **1907**, p. 158.

[5] Timmermans, *Z. Elektrochem.*, **12**, 644 (1906); *Z. physik. Chem.*, **58**, 129 (1907).

alcohol-solvent-water mixtures.[6] Anhydrous methyl alcohol was prepared from pure methyl alcohol of commerce by the usual treatment with lime. Samples of alcohol containing various amounts of water were made up from this anhydrous alcohol, the exact amount of water present being determined by specific-gravity measurements. These samples were sealed and set aside for solution-temperature readings.

Careful study was given to the selection of a suitable solvent. Such a solvent must be miscible with alcohol to a degree, but not completely miscible at all temperatures. It may have a boiling point higher than that of methyl alcohol, but not much lower. Since methyl alcohol boils at 66° the solution temperatures of the alcohol-solvent-water mixture should range from 60°, to, for convenience, 0°. A number of solvents were tried by us, including chloroform, kerosene, carbon disulfide, benzene, nitrobenzene, a mixture of benzene and ligroin and ligroin. Low-boiling ligroin was found to show the best range of solution temperatures. Ligroin tends to change in composition if kept for frequent use over a long period of time, due to unequal rates of evaporation of the various ingredients. This difficulty was largely obviated by a distillation of the low-boiling ligroin into several fractions, each of which was collected over a range of five degrees. Of these fractions the one boiling at 50–55° was chosen.[7]

Several liters of the low-boiling ligroin were thoroughly dried over fresh sodium wire and then distilled from the sodium, the fraction boiling at 50–55° being collected in small dry containers which were sealed as soon as filled. Such a distillate can be kept for some time without important change in composition due to evaporation.

The solution-temperature observations were made according to the following procedure: two parts by volume of ligroin of 50–55° boiling point to one part by volume of the methyl alcohol to be tested are brought into a test-tube, each reagent being measured from a dry pipet. The homogeneous mixture is cooled until the appearance of a cloudiness. A thermometer is placed in the solution, which is allowed to grow warm rather gradually to the temperature at which the second phase disappears. The temperature at which the solution again becomes homogeneous is recorded as the solution temperature. It is noteworthy that the temperature at which the second liquid phase appears when the homogeneous mixture is slowly cooled is identical with that at which it disappears when the cloudy solution is slowly warmed.

Cols. 2, 3 and 4 of Table I contain the results of the work so far discussed. The contents of Col. 5 will be explained later.

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[6] See Bur. Standards *Bull.*, 9, 345 (1913), for a discussion of somewhat similar work with ethyl alcohol.

[7] Crismer also used ligroin as the solvent for methyl alcohol in his work but of a higher boiling point than that selected by us.

TABLE I

WATER CONTENT AND SOLUTION TEMPERATURES OF METHYL ALCOHOL (1 VOL.) WITH LIGROIN (2 VOL., B. P. 50–55°C.) AND WITH HEXANE (2 VOL.)

1 Sample of CH_3OH	2 d_4^{15}[a]	3 Purity[b]	4 Soln. temp., °C. ligroin, b. p. 50–55° as solv.	5 Soln. temp., °C. hexane, b. p. 68.6–69.0° as solv.
1	0.79578	100.00	8.65	36.55
2	.79634	99.80	10.70	37.90
3	.79676	99.65	12.05	38.95
4	.79718	99.50	13.90	40.05
5	.79760	99.35	15.35	41.00
6	.79810	99.18	17.00	42.05
7	.79845	99.05	18.25	43.00
8	.79947	98.69	21.55	45.00
9	.80016	98.56	22.80	45.55
10	.80026	98.41	23.65	46.25
11	.80058	98.30	24.95	46.90
12	.80140	98.01	27.15	48.05
13	.80165	97.92	27.90	48.50
14	.80292	97.48	30.90	50.15
15	.80390	97.13	33.20	51.10
16	.80407	97.07	33.75	...
17	.80488	96.79	35.60	...
18	.80590	96.43	37.50	...
19	.80673	96.13	39.10	...
20	.80698	96.05	39.55	...

[a] Determinations were made with an Ostwald pycnometer upon air-saturated alcohol.

[b] Expressed in parts in one hundred of alcohol. Water regarded as the impurity.

The data in Cols. 3 and 4 are conveniently recorded in the accompanying graph, which shows the variation in water content of the alcohol with change in solution temperature. By reference to Curve I the water content of any sample of alcohol containing not more than 4% of water may be determined, providing the solution temperature of the sample with ligroin of 50–55° boiling point is known.

Curve I has been used for this purpose in this Laboratory. It is obvious that the curve will reach a limit of usefulness, however, when the supply of ligroin used in accumulating data for the curve is exhausted. Since the ingredients of ligroin from different sources vary considerably, it will become necessary to obtain a new set of solution-temperature data when a new batch of solvent has been prepared.

The method under discussion was standardized and its usefulness enhanced by the use as solvent of pure synthetic normal hexane of boiling point 68.6–69.0° (uncorr.) at atmospheric pressure. Hexane is the chief ingredient of low-boiling ligroin. The use of a pure solvent afforded a standard and permanent set of solution-temperature data. Solution-temperature determinations were made upon mixtures of hexane (two volumes) with samples of methyl alcohol (one volume) containing measured amounts of water by exactly the same procedure as with ligroin. The solution temperatures of the alcohol-water-hexane system are recorded in Col. 5 of the table. The relation of variation of water content of the alcohol to change in solution temperature is shown in Curve II. By consulting Curve II, the water content of any sample of alcohol containing not more than 3% of water may be determined, providing the solution temperature of that sample with hexane is known.

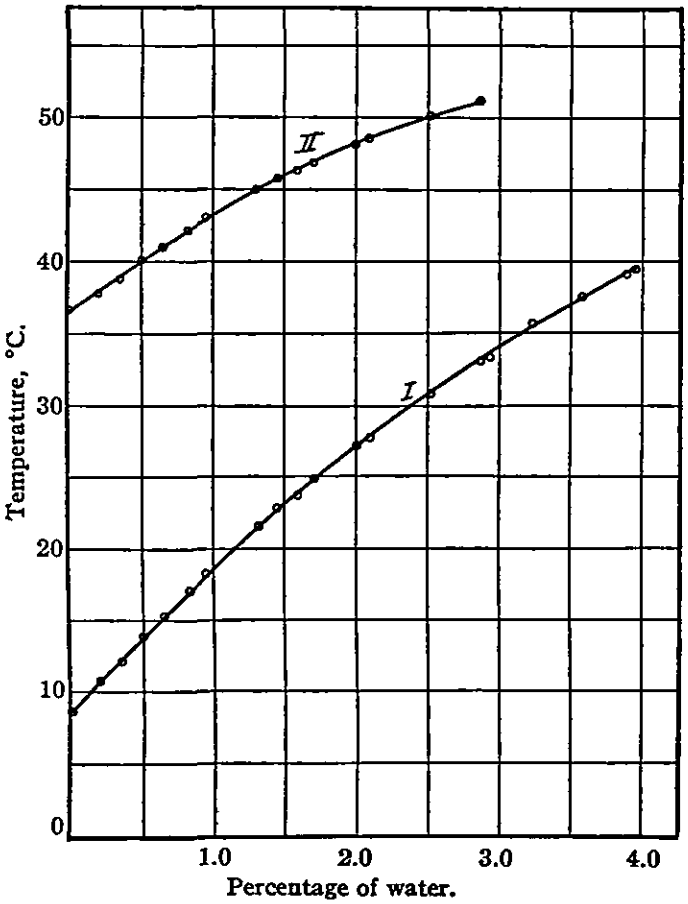

Fig. 1.—Curve I. Water content and solution temperatures of methyl alcohol (1 vol.) with ligroin (2 vol., b. p. 50–55°). Curve II. Water content and solution temperatures of methyl alcohol (1 vol.) with hexane (2 vol.).

It will be observed that the range of solution temperatures with ligroin is 31° for 4% of water, and with hexane over 15° for 3% of water. These are sufficiently wide ranges to make the method a delicate one, and this feature is therefore worthy of particular emphasis.

Summary

1. This paper describes an application of Crismer's method for measuring quantitatively the amount of water in methyl alcohol.

2. The method is based upon the determination of solution temperatures of the three component systems methyl alcohol-water-ligroin, and methyl alcohol-water-hexane; the exact amount of water present in a given case is determined, once for all, by specific-gravity measurements.

3. The wide range of solution temperatures observed with the two solvents used makes the method accurate and sensitive.

4. The use of pure hexane as solvent is recommended, since by its use a set of permanent data can be obtained.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE DIVISION OF BIOCHEMISTRY AND PHARMACOLOGY, UNIVERSITY OF CALIFORNIA MEDICAL SCHOOL]

OBSERVATIONS UPON THE SYNTHESIS OF PYRROLE- AND PYRROLIDONE-CARBOXYLIC ACIDS, AND UPON THE SYNTHESIS OF ALPHA-THIONIC ACID OF PYRROLE[1]

BY C. M. MCCAY AND CARL L. A. SCHMIDT

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Introduction

One of the problems which continually confront biochemists is the lack of a satisfactory supply of the constituents of the protein molecule. With the exception of glutamic acid[2] which is used in Japan as a condiment the production of the amino acids is extremely limited. In certain instances the known methods of preparation are such as to yield products of doubtful purity. This is particularly true of the amino acids which contain the pyrrole ring. While our attempts to synthesize proline have been unsatisfactory some additional information regarding the behavior of certain of the pyrrole compounds has been gained.

The two methods for the synthesis of proline which are best known are those of Sörensen[3] and of Fischer and Zemplén.[4] The former carried out his synthesis by permitting the diethyl ester of sodium phthalimidomalonic acid to react with trimethylene-bromide with the formation of α-bromopropyl-phthalimidomalonic ester. When this substance is boiled with potassium hydroxide, proline, glycine and a number of other products

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[1] This investigation has been aided by a grant from the Research Board of the University of California.

[2] Ikeda, Eighth Intern. Cong. Appl. Chem., 18, 147 (1912). Ikeda and Suzuki, U. S. pat. 1,015,891, 1,035,591 (1912). Schmidt and Foster, *Proc. Soc. Exptl. Biol. Med.*, 18, 205 (1921).

[3] Sörensen, *Compt. rend. trav. lab. Carlsberg*, 6, 137 (1905).

[4] Fischer and Zemplén, *Ber.*, 42, 1022, 2989 (1909).

result. This synthesis is expensive due to the cost of the initial products. The Fischer and Zemplén synthesis involves the breaking of the piperidine ring by oxidation with potassium permanganate, which yields benzoyl-*d*-aminovalerianic acid. The latter substance is brominated and then boiled with alkali. In both syntheses proline is contaminated with secondary products of the reaction which are very difficult to remove.

Experiments with Pyrrolidone-α-Carboxylic Acid

Pyrrolidone-α-carboxylic acid affords a possible source for the synthesis of proline. This product is readily formed from glutamic acid by heating at 150–160°,[5] and in turn it is easily hydrolyzed to glutamic acid by boiling with concd. hydrochloric acid.[6] Fischer and Boehner[7] saw in pyrrolidone-α-carboxylic acid a possible source for proline and their work consisted in an attempt to reduce the ethyl ester of this substance by means of sodium and alcohol. The yield, however, was extremely poor. The following reagents were used by us in our attempts to reduce pyrrolidone-α-carboxylic acid: zinc amalgam, tin and hydrochloric acid, sodium and ethyl alcohol, sodium amalgam and water, aluminum and sodium hydroxide, aluminum amalgam, and phosphorus and hydriodic acid in sealed tubes. Catalytic reduction was tried with platinum as a catalyst[8] using water, glacial acetic acid and alcohol as solvents and hydrogen under pressure of one atmosphere. The catalytic reductions were attempted at both room temperatures and 100°. In no instance was there a measurable reduction.

Attempts were also made to induce the carbonyl group of the pyrrolidone compound to react with phenylhydrazine and hydroxylamine but without success. Negative results were also obtained in the attempts to reduce the ethyl ester of the pyrrolidone compound with platinum as a catalyst.

Experiments with the α-Carboxylic Acid of Pyrrole

A series of experiments was next carried out in an effort to reduce the amide of the α-carboxylic acid of pyrrole. Fischer[9] attempted this reduction, using phosphonium iodide and hydriodic acid but found he could obtain only pyrroline-α-carboxylic acid. In our experiments the amide was prepared by the method of Schwanert.[10] Catalytic reduction was attempted with hydrogen in the presence of platinum and palladium. Various strengths of alcohol with and without the addition of different amounts of hydrochloric acid were employed as solvents. No reduction

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[5] Haitinger, *Monatsh.*, 3, 228 (1882).

[6] Foreman, *Biochem. J.*, 8, 481 (1914).

[7] Fischer and Boehner, *Z. physiol. Chem.*, 65, 118 (1910).

[8] Prepared both by the methods of Adams and Kaufmann, THIS JOURNAL, 45, 3029 (1923), and Willstätter and Hatt; *Ber.*, 45, 1472 (1912).

[9] Fischer and Van Slyke, *Ber.*, 44, 3166 (1911). Fischer and Gerlach, *Ber.*, 45, 2453 (1912).

[10] Schwanert, *Ann. Chem. Pharm.*, 116, 270 (1860).

was obtained when pyromucic acid was added to the flask, indicating that the catalyst had been poisoned. A control experiment with pyromucic acid alone showed that this substance readily absorbed hydrogen.

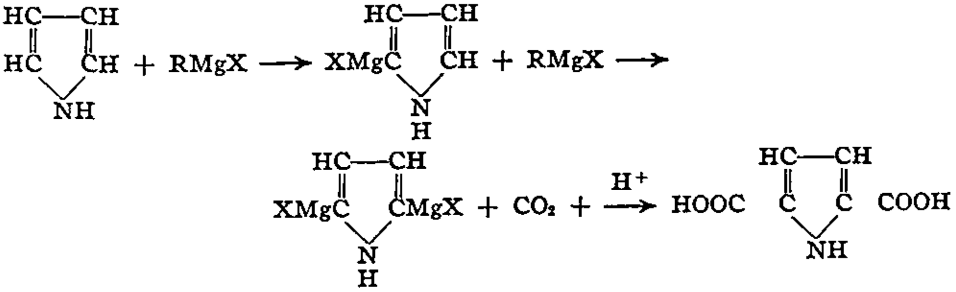
Synthesis of the α-Carboxylic Acid of Pyrrole

Another source for the α-carboxylic acid of pyrrole was found in the method developed by Oddo,[11] and the later improvement of Gilman and Pickens.[12] They obtained the acid by passing carbon dioxide through an ether solution of pyrrylmagnesium iodide and decomposing the resulting compound with sulfuric acid. Oddo reports a yield of 25–30%. Since a better yield is desirable we found it advantageous to modify the conditions of preparation.

Methylmagnesium iodide was prepared according to the optimum conditions which have been developed for the Grignard reagent by Gilman.[13] Our reagent was found to be 0.62 *N*. From a large number of runs we found that the following gave the best yield. A solution of 10 cc. of pyrrole in 100 cc. of absolute ether was slowly added during rapid stirring to 338 cc. of the Grignard reagent. The mixture was cooled with ice, and carbon dioxide was slowly passed through the flask for an hour. An excess of normal sodium hydroxide solution was added, the mixture heated to boiling and the resulting magnesium hydroxide removed by filtration. The filtrate was treated with charcoal, concentrated to a small volume, cooled and sufficient hydrochloric acid was added to make the reaction just acid to litmus. A large proportion of the desired product was separated at this point. The supernatant liquid was further acidified and the last traces of the product were extracted with ether. The yield was 6.46 g., or 40%.

These studies to obtain a maximum yield throw some light upon the mechanism of the reaction. The optimum molecular proportion for the synthesis of pyrrylmagnesium iodide is one of pyrrole to 1.4 of methylmagnesium iodide. If an amount of the latter substance in excess of this ratio is employed, it is used up in the formation of acetic acid.

It might be expected that, instead of the reaction proceeding up to the extent of about 40% of the available pyrrole and the excess of any available methylmagnesium iodide being converted into acetic acid, the reaction might proceed as follows.



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[11] Oddo, *Gazz. chim. ital.*, **39**, I, 649 (1909); **44**, I, 482 (1914); *Ber.*, **43**, 1012 (1910).

[12] Gilman and Pickens, This Journal, **47**, 245 (1925).

[13] Gilman, *ibid.*, **45**, 154 (1923).

The products of this reaction should be α,α'-dicarboxylic acid of pyrrole as well as α-carboxylic acid of pyrrole and acetic acid. The recent work of Dufford[14] and his co-workers on the luminescence of Grignard compounds when exposed to the action of a stream of oxygen might throw some light upon the position of the —MgI group in pyrrylmagnesium iodide. When a stream of oxygen was allowed to play on the surface of a solution of pyrrylmagnesium iodide, no luminescence was observed. In view of Dufford's experiments these results may, indicate that the —MgI remains on the nitrogen until carbon dioxide has been blown into the solution. In the light of the more recent experiments of Evans and Diepenhorst[15] however, this can but little more than confirm the conclusions of the previous observation in which it was noted that α,α'-dicarboxylic acid of pyrrole is not obtained even when a large excess of methylmagnesium iodide is used in the preparation of pyrrylmagnesium iodide.

Further Attempts to Reduce the α-Carboxylic Acid of Pyrrole

Using the α-carboxylic acid of pyrrole which was synthesized by the Grignard method, numerous attempts at catalytic reduction were made. The same solvents as those previously mentioned were used. In contrast to the earlier attempts the catalyst was never poisoned as was shown by its ability to reduce xylene. In only one case was hydrogen absorbed, in a 50% solution of alcohol containing 2 cc. of concd. hydrochloric acid, and 1.7 g. of the α-carboxylic acid of pyrrole. More than the calculated amount necessary for complete reduction was absorbed, using the platinum oxide catalyst. The resulting solution did not blacken in air. It was thoroughly extracted with ether and only a trace of the original was found in the ether extract. After careful neutralization with sodium hydroxide the solution was evaporated in a vacuum to dryness. The dried residue was thoroughly extracted with absolute alcohol. The brown alcoholic solution, when evaporated to dryness, left a dark residue which resembled proline before it crystallizes. Sörensen[16] has called attention to the use of phosphotungstic acid as a qualitative test for proline. The alcoholic residue was dissolved in water and treated with phosphotungstic acid. A voluminous white precipitate resulted. Attempts were made to identify this residue but failed on account of the small amount of material available. The evidence, however, did not indicate that the substance was either proline phosphotungstate whose nitrogen content was found to be 1.1%, or pyrrolidine tungstate which when prepared under identical conditions gave a nitrogen value of 1.3%. More studies upon this compound are in progress.

[14] Dufford, Nightingale and Calvert, This Journal, 47, 95 (1925). Evans and Dufford, *ibid.*, 45, 278 (1923). Dufford, Calvert and Nightingale, *ibid.*, 45, 2058 (1923).

[15] Evans and Diepenhorst, This Journal, 48, 715 (1926).

[16] Sörensen, *Compt. rend. trav. lab. Carlsberg*, 6, 137 (1905). McCay and Schmidt, *J. Gen. Physiol.*, 9, 333 (1926).

E. Fischer[17] has previously described the phenylhydantoin as the best derivative to characterize proline. Following his directions the proline derivative was readily prepared from a solution of pure proline while the unknown residue yielded brown, feather-shaped crystals of indefinite melting point.

Incidental observations showed that the oxidation of the α-carboxylic acid of pyrrole to form melanin-like compounds is dependent upon the hydrogen-ion concentration of the solution. Alkaline solutions can be boiled for some time without the least darkening, while solutions acidified with hydrochloric acid when exposed to the air at room temperatures turn black in several hours. No darkening was observed in acidified solutions when kept in an atmosphere of hydrogen, even after a period of six months.

The Reaction between Methylmagnesium Iodide and Pyrrolidine

Experiments were also carried out to determine whether methylmagnesium iodide reacts with pyrrolidine in the same manner as it does with pyrrole. Accordingly 5 g. of pyrrolidine was treated with the calculated amount of methylmagnesium iodide. The evolution of methane showed that it reacted in the manner customary to secondary amines. After carbon dioxide was blown through the reagent in the usual manner, it was acidified with sulfuric acid and extracted with ether. The ether extract contained a considerable amount of pyrrolidine. The acid was removed from the ether-extracted solution before it was evaporated to dryness in a vacuum. A slight, black residue resulted which was found to contain no proline.

These experiments indicate that in the saturated pyrrolidine ring the —MgX portion of the Grignard reagent does not migrate to the alpha position under the experimental conditions employed here. Since it remains attached to the nitrogen it is removed by the subsequent treatment with carbon dioxide and a strong acid.

Synthesis of the α-Dithionic Acid of Pyrrole

Since pyrrole itself is readily oxidized by the oxygen of the air we might expect any compound containing both it and thio groups to be very readily subject to oxidation. No such compounds are known and it is possible that if prepared they would possess considerable interest.

Houben[18] was the first to employ the Grignard reagent for the synthesis of dithionic acids. He treated RMgX compounds with carbon disulfide in place of carbon dioxide and obtained the resulting substances which he called carbithionic acids. In more recent times a number of these acids have been produced by treating aldehydes with ammonium polysulfide.[19] A search of the literature reveals no such acid in which a pyrrole nucleus or a nitrogen atom is involved in a nucleus that holds a dithionic acid group.

[17] Fischer, *Z. physiol. Chem.*, **88**, 189 (1913).

[18] Houben, *Ber.*, **39**, 3219 (1906).

[19] Bruni and Levi, *Atti. accad. Lincei*, **32**, 5 (1923).

The synthesis of α-dithionic acid of pyrrole was carried out as follows. The methylmagnesium iodide was prepared using 26.7 g. of magnesium and 156 g. of methyl iodide in 500 cc. of absolute ether. To this solution was added 67 g. of pyrrole in 500 cc. of absolute ether. Sixty g. of carbon disulfide was then added while the pyrrylmagnesium iodide was well stirred.

After the addition of the carbon disulfide an excess of sodium hydroxide was added, the solution was heated to boiling and extracted four times with fresh ether. The black precipitate of magnesium hydroxide was then filtered off with suction. A considerable amount of the product was recovered from the precipitate by boiling up several times with water, filtering and adding to the main portion of the solution. The solution of the sodium salt was concentrated to a small volume and acidified with sulfuric acid. The reddish oil that was thus set free was again extracted with ether in which it was readily soluble. The ether solution was dried over sodium sulfate. A portion was evaporated to dryness in a vacuum desiccator. This left a dark brown oil which later turned to a (partly crystalline) pasty mass. This solid was almost completely soluble in alkali and ether. It was only slightly soluble in acid and practically completely soluble in chloroform, ethyl alcohol and carbon disulfide.

Five-cc. portions of the ether solution were titrated in water with phenolphthalein as an indicator. Because of the color of the thionic acid the end-point was rather difficult to distinguish. The titration with sodium hydroxide solution showed an approximate yield of 40%. A portion of the ether solution of the acid was added to a large excess of water. This was divided into three portions and served for the preparation of the iron, mercury and lead salts. These were precipitated upon the addition of ferrous chloride and the acetates of mercury and lead, respectively. The iron salt formed a deep green precipitate which turned black in the air. The rate of blackening was much increased by exposure to sunlight. The mercury salt formed a light yellow, colloidal solution which was precipitated as a yellow salt upon boiling. The lead salt was a deep red and precipitated readily.

Attempts were made to find a solvent for recrystallizing the lead salt, but it seemed practically insoluble in all the ordinary solvents. This may prove a method for the quantitative determination of lead. It was only slightly soluble in boiling acetone. The lead salt was dried for three hours at 110° in the electric oven. Nitrogen was determined in the salt by the Kjeldahl method and the sulfur by a modification of the Carius method. The latter had to be modified, due to the fact that a lead salt was being analyzed. The lead salt was heated in a sealed tube with nitric acid for the usual length of time. At the conclusion, half the sulfur was present as lead sulfate. This was dissolved in ammonium acetate and precipitated with barium nitrate. The method of precipitation with barium nitrate is known to give high results and hence is not usually employed. In both cases the sulfur analyses were too high and the checks were poor.

Anal. Calcd.: N, 5.7; S, 26.1. Found: N, 5.5, 5.5; S, 27.7, 28.7.

The α-dithionic acid of pyrrole was easily oxidized to a black powder when exposed to the air. Its solution was also readily blackened by light. The compound reacted with benzoyl chloride to give a precipitate of black shining crystals.

Summary

1. Attempts to synthesize proline by reduction of pyrrolidone-α-carboxylic acid and the α-carboxylic acid of pyrrole are described, all of which yielded negative results.

2. Considerable information concerning the synthesis of pyrrole-α-carboxylic acid with the aid of the Grignard reagent has been accumulated.

The luminescence of unsaturated compounds was used to throw additional light on the structure of pyrrylmagnesium iodide.

3. The reaction between pyrrolidine and methylmagnesium iodide has been studied. It has been shown that the —MgX group does not migrate to the alpha position under the experimental conditions studied.

4. The synthesis of the α-dithionic acid of pyrrole is described.

BERKELEY, CALIFORNIA

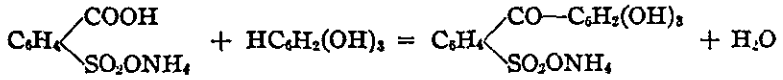
[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

PYROGALLOLSULFONEPHTHALEIN, SULFONEGALLEIN, 2,3,4-TRIHYDROXY-BENZOYL-BENZENE-ORTHO-SULFONIC ACID (THE INTERMEDIATE ACID), AND SOME OF THEIR DERIVATIVES

BY W. R. ORNDORFF AND NATHANIEL FUCHS[1]

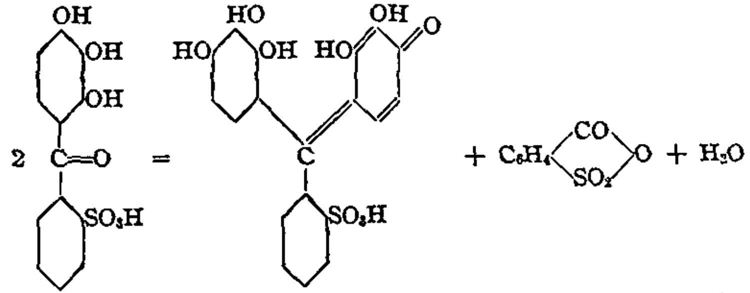
RECEIVED JANUARY 15, 1926 PUBLISHED JULY 6, 1926

The ammonium salt of 2,3,4-trihydroxy-benzoyl-benzene-*o*-sulfonic acid was prepared by heating the acid ammonium salt of *o*-sulfobenzoic acid with pyrogallol.

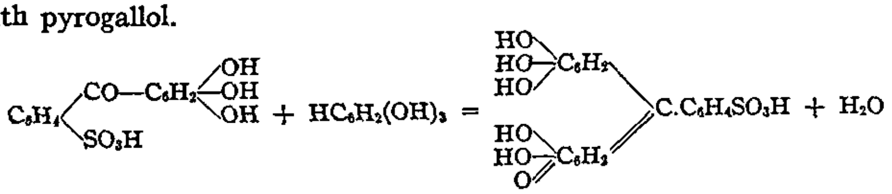


$$C_6H_4\left\langle\begin{matrix}COOH\\SO_2ONH_4\end{matrix}\right. + HC_6H_2(OH)_3 = C_6H_4\left\langle\begin{matrix}CO-C_6H_2(OH)_3\\SO_2ONH_4\end{matrix}\right. + H_2O$$

The free acid was obtained by passing dry hydrogen chloride into the ammonium salt suspended in absolute ethanol. When heated alone at 140°, it forms pyrogallolsulfonephthalein, *o*-sulfobenzoic anhydride and water.



Pyrogallolsulfonephthalein also results when the trihydroxy acid is heated with pyrogallol.



$$C_6H_4\left\langle\begin{matrix}CO-C_6H_2\left\langle\begin{matrix}OH\\OH\\OH\end{matrix}\right.\\SO_3H\end{matrix}\right. + HC_6H_2(OH)_3 = \begin{matrix}\begin{matrix}HO\\HO\\HO\end{matrix}\Big\rangle C_6H_2\\ \begin{matrix}HO\\HO\\O\end{matrix}\Big\rangle C_6H_2\end{matrix}\Big\rangle C.C_6H_4SO_3H + H_2O$$

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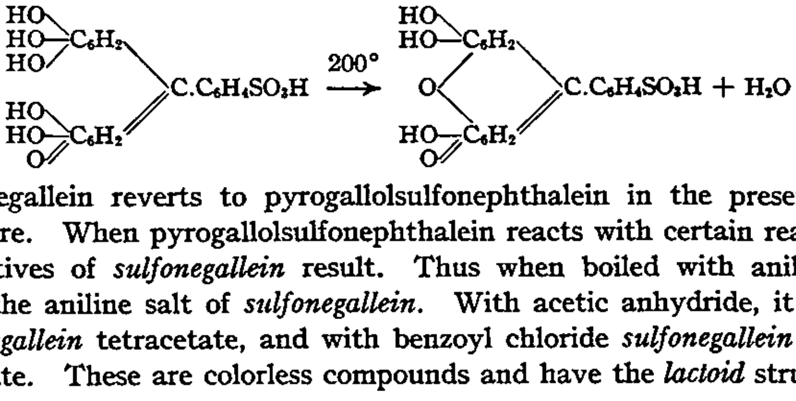
[1] This article is based on a thesis submitted to the Faculty of the Graduate School of Cornell University by Nathaniel Fuchs, Grasselli Fellow in Chemistry, in partial fulfilment of the requirements for the degree of Doctor of Philosophy. An abstract of this paper was presented at the seventieth meeting of the American Chemical Society at Los Angeles, in 1925.

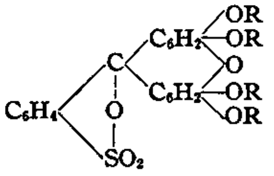
Hence the trihydroxy acid is called the intermediate acid. Pyrogallolsulfonephthalein is best made by heating *o*-sulfobenzoic acid anhydride with pyrogallol at 135–140°, with zinc chloride. The reaction takes place in two steps: first one molecule of pyrogallol combines with one of the anhydride to give the trihydroxy acid, and then this acid reacts with more pyrogallol to form the sulfonephthalein as shown above. The sulfonephthalein was also obtained by heating pyrogallol with saccharin and sulfuric acid, or with the chlorides of *o*-sulfobenzoic acid.

Pyrogallolsulfonephthalein reacts as a tautomeric substance, forming colored, *quinoid* and colorless *lactoid* derivatives. The compound itself is colored, has the *quinoid* form and is an inner carbonium or oxonium salt. As a monobasic acid it forms highly-colored salts. It also reacts as a polybasic acid as shown by the zinc and the lead salts.

When heated to 200° pyrogallolsulfonephthalein loses a molecule of water and gives sulfonegallein.



Sulfonegallein reverts to pyrogallolsulfonephthalein in the presence of moisture. When pyrogallolsulfonephthalein reacts with certain reagents, derivatives of *sulfonegallein* result. Thus when boiled with aniline, it gives the aniline salt of *sulfonegallein.* With acetic anhydride, it forms *sulfonegallein* tetracetate, and with benzoyl chloride *sulfonegallein* tetrabenzoate. These are colorless compounds and have the *lactoid* structure.



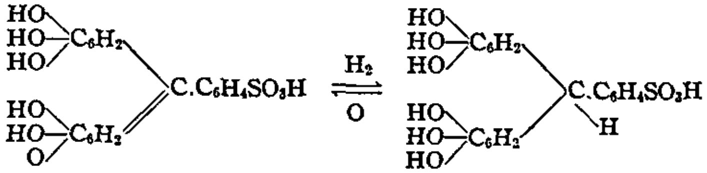
where R = $COCH_3$ or COC_6H_5

They are hydrolyzed by dilute alkalies, showing at first a green fluorescence, which is soon replaced by a blue color.

Pyrogallolsulfonephthalein forms a brick-red, monomethyl ether, and a red trimethyl ether. The dimethyl ether of *sulfonegallein* occurs in two modifications, one consisting of orange, rectangular tablets and the other of red, triangular plates. Both crystallize in the rhombic system. As *all* of these ethers are colored they have the *quinoid* structure.

Pyrogallolsulfonephthalein yields a *colored* dibromo derivative, which is also tautomeric, having for itself and its ammonium salt the *quinoid* structure, and forming a *colorless* tetrabenzoate of *dibromosulfonegallein* which has the *lactoid* structure.

On reduction with zinc dust and water, pyrogallolsulfonephthalein is converted into the colorless zinc salt of pyrogallolsulfonephthal*in*. Pyrogallolsulfonephthal*in* is very readily oxidized back to pyrogallolsulfonephthalein.



The sulfonephthal*in* differs from the sulfonephthalein in being readily soluble in water.

Experimental Part[2]

The Ammonium Salt of 2,3,4-Trihydroxy-benzoyl-benzene-*o*-sulfonic Acid.—Two hundred g. of the acid ammonium salt of *o*-sulfobenzoic acid[3] was heated with 115 g. of pyrogallol. The fused mass, after being heated at 190–195° for an hour, became solid. Three crystallizations of the light orange-red product from hot water gave colorless prisms. The yield was 68%. Analyses[4] of the air-dried crystals showed that they were the ammonium salt of trihydroxy-benzoyl-benzene-*o*-sulfonic acid with 0.25 molecule of water of crystallization.

Anal. Subs., 0.4807, 0.5971: loss at 120°, H_2O, 0.0065, 0.0082. Calcd. for $C_{13}H_{10}O_7SNH_3 + 0.25\ H_2O$: H_2O, 1.36. Found: 1.35, 1.37.

Subs. (dry), 0.5555, 0.5555, 0.5971: cc. of 0.1 N H_2SO_4, 16.94, 16.75, 17.92. Subs. (dry), 0.5889: $BaSO_4$, 0.4120. Calcd. for $C_{13}H_{10}O_7SNH_3$: NH_3, 5.20; S, 9.80. Found: NH_3, 5.19, 5.14, 5.11; S, 9.61.

The ammonium salt is practically insoluble in most of the usual organic solvents, but dissolves somewhat in methanol and in ethanol and is very soluble in hot water. When heated in a melting-point tube, it begins to turn dark at 296° and melts sharply to a red liquid at 298°.

2,3,4-Trihydroxybenzoyl-benzene-*o*-sulfonic Acid.—Fifty g. of the ammonium salt was suspended in 300 cc. of absolute ethanol. Dry hydrogen chloride was passed into the suspension for six hours. The ammonium salt of the trihydroxy acid dissolved and ammonium chloride was precipitated. The alcohol solution was filtered and concentrated, but no crystals could be obtained. When all the alcohol was removed, a sticky, brownish mass remained. This was thoroughly dried on the water-bath in a vacuum and then left in a vacuum desiccator for a few days. It crystallized slowly into a cream-colored solid. The material was powdered and recrystallized five times from concd. hydrochloric acid. In this way, light yellow crystals were obtained. They begin to soften at 103° and melt to a yellow-brown liquid at 108–109°. Analyses of the air-dried product showed that it was trihydroxy-benzoyl-benzene-*o*-sulfonic acid with 3 molecules of water of crystallization, but the water could not be determined by drying because the acid changed into pyrogallolsulfonephthalein, *o*-sulfobenzoic acid anhydride and water when heated.

Anal. Subs, 0.3562, 0.2966: $BaSO_4$, 0.2284, 0.1918. Calcd. for $C_{13}H_{10}O_7S + 3H_2O$: S, 8.80. Found: 8.81, 8 88.

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[2] We are indebted to the Monsanto Chemical Works of St. Louis for the saccharin used in this investigation.

[3] Blackshear, *Am. Chem. J.*, **14**, 455 (1892).

[4] International Atomic Weights for 1925 are used in the computations in this paper.

The molecular weight of the acid with 3 molecules of water was determined by titration with 0.1 *N* sodium hydroxide solution. With methyl red it titrates as a *monobasic* acid.

Mol. Wt. Subs., 0.2117, 0.5290: cc. of 0.1 *N* NaOH, 5.83, 14.46. Calcd. for $C_{13}H_{10}O_7S + 3H_2O$: mol. wt., 364.2. Found: 363.1, 365.8.

It titrates as a *dibasic* acid, however, with phenolphthalein.

Mol. Wt. Subs., 0.2117, 0.3640: cc. of 0.1 *N* NaOH, 11.61, 19.91. Calcd. for $C_{13}H_{10}O_7S + 3H_2O$: mol. wt., 364.2. Found: 364.7, 365.6.

*The acid is very soluble in water, ethanol and ethyl acetate, and is practically in*soluble in ether, benzene and chloroform.

TRIBENZOATE.—The benzoate was made by boiling the acid with benzoyl chloride. The excess of benzoyl chloride was evaporated in a current of carbon dioxide in a water oven. The product could not be crystallized, but was purified by dissolving it in ether and precipitating with petroleum ether. The colorless flocculent precipitate was precipitated twice again in the same way. The analysis below, made on the product after it had been kept in a vacuum desiccator for ten days, showed that it was the tribenzoate; m. p., 62–64°.

Anal. Subs., 0.4834: $BaSO_4$, 0.1845. Calcd. for $C_{13}H_7O_7S\ (COC_6H_5)_3$: S, 5.15. Found: 5.24.

Pyrogallolsulfonephthalein

Preparation of Pyrogallolsulfonephthalein. (1) *By Heating 2,3,4-Trihydroxybenzoyl-benzene-o-sulfonic Acid.*—Five g. of the pure acid was heated for six hours at 140°. The mass turned green and colorless needles of the anhydride of *o*-sulfobenzoic acid sublimed. The crystalline pyrogallolsulfonephthalein was recrystallized by dissolving it in hot, dil. sodium hydroxide solution and acidifying with hydrochloric acid. Two g. of green crystals was obtained. The material was dried at 130°.

Anal. Subs. (dry), 0.4362: $BaSO_4$, 0.2415. Calcd. for $C_{19}H_{14}O_9S$: S, 7.67. Found S, 7.60.

(2) *From 2,3,4-Trihydroxybenzoyl-benzene-o-sulfonic Acid and Pyrogallol.*—Five g. of the pure acid was heated with 2 g. of pyrogallol at 135–145°. The red liquid became a green solid after being heated for six hours. The sulfonephthalein was recrystallized as above. The air-dried sample was analyzed.

Anal. Subs., 0.3452: loss at 130°, 0.0021. Subs. (dry), 0.3431: $BaSO_4$, 0.1904. Calcd. for $C_{19}H_{14}O_9S$: S, 7.67. Found: S, 7.62.

(3) *From the Anhydride of o-Sulfobenzoic Acid and Pyrogallol.*—Seventy-five g. of *o*-sulfobenzoic acid anhydride and 113 g. of pyrogallol were heated at 130–135° for 20 hours. The mixture was treated with hot water thrice and filtered. The finely-crystalline, reddish-brown sulfonephthalein had a green surface color; yield, 51%. The same yield was obtained by running a condensation at 135–140° for 18 hours or for *30 hours. By using zinc chloride and heating at 135–140°, the same yield was obtained,* but the time required was reduced to eight hours and the product consisted of larger crystals much more easily purified. Pyrogallolsulfonephthalein is best made in this way.

The product was purified by dissolving in sodium hydroxide solution and precipitating with hydrochloric acid. A second recrystallization in the same way gave dark green crystals which ground to a red powder. They were allowed to dry in the air for a week and analyzed.

Anal. Subs., 0.2304, 0.2423; loss at 130°, 0.0017, 0.0019. Subs. (dry), 0.2287, 0.2404: CO_2, 0.4570, 0.4791; H_2O, 0.0715, 0.0747. Subs. (dry), 0.5118, 0.6470; $BaSO_4$, 0.2806, 0.3594. Calcd. for $C_{19}H_{14}O_9S$: C, 54.52; H, 3.37; S, 7.67. Found: C, 54.50, 54.35; H, 3.50, 3.48; S, 7.53, 7.63.

These analyses prove that pyrogallolsulfonephthalein has the formula $C_{19}H_{14}O_9S$ and not $C_{19}H_{10}O_8S$ as stated by Sohon.[5]

(4) *From the Chlorides of o-Sulfobenzoic Acid and Pyrogallol.*—Ten g. of the chlorides and 13.5 g. of pyrogallol were heated six hours at 145°. Hydrogen chloride was given off. The product was dissolved in sodium hydroxide solution. The deep blue alkaline solution treated with hydrochloric acid gave 6 g. of green crystals of pyrogallolsulfonephthalein.

About 1 g. did not dissolve in the sodium hydroxide solution. When this substance was crystallized from benzene, colorless, transparent crystals, which melted at 109–111° and boiled in the melting point tube at about 230° were obtained. From analogy with the other esters of *o*-sulfobenzoic acid, which were obtained as by-products in the condensation of phenols with the chlorides of *o*-sulfobenzoic acid, it appears that the product is the *dipyrogallyl ester of o-sulfobenzoic acid*, $(OH)_2C_6H_3OCO.C_6H_4.SO_2OC_6H_3(OH)_2$.

(5) *From Saccharin, Sulfuric Acid and Pyrogallol.*—Twenty g. of saccharin, 25 g. of concd. sulfuric acid and 30 g. of pyrogallol were heated together at 135–145° for six hours. Water was added and the green crystals of pyrogallolsulfonephthalein recrystallized in the usual way; yield, 20%.

Anal. Subs. (dried at 130°), 0.5146; $BaSO_4$, 0.2856. Calcd. for $C_{19}H_{14}O_9S$: S, 7.67. Found: 7.62.

Properties and Crystalline Form.—Pyrogallolsulfonephthalein is insoluble in most organic solvents. It dissolves somewhat in water, methanol, ethanol and formic acid (85%) forming a red solution. In cold water it dissolves to the extent of one g. in about 20 liters and it is about three times as soluble in boiling water. Sodium hydroxide or sodium carbonate solutions dissolve it very readily, producing in very dilute solutions of the alkali a deep red color (monosodium salt) and in stronger solutions a very deep blue color (polysodium salt). Sodium bicarbonate solution gives only the deep red color of the monosodium salt. In very dilute aqueous ammonia solution a red color is obtained, changing to a purple as the concentration of ammonia is increased. Acids precipitate the pyrogallolsulfonephthalein from these solutions. The color changes at different hydrogen-ion concentrations are given in the table below. The colors were judged by comparison with the color chart found in Mulliken's "Identification of Pure Organic Compounds," Vol. 1.

*P*H	2.0	3.0	4.0	5.0	6.0–10.0	11.0	12.0
Color	YO_1	YO_1	RO_1	R_1	VR_1	RV_1	VB_1

In alkaline solutions stronger than *P*H = 8, the color fades rapidly due to oxidation. None of the solutions of pyrogallolsulfonephthalein show fluorescence.

Pyrogallolsulfonephthalein does not melt below 315°. It dissolves in concd. sulfuric acid forming a red solution and is precipitated in a red form when the solution is poured into water. Unlike pyrogallolbenzein,[6] it does not absorb hydrogen chloride, indicating that pyrogallolsulfonephthalein should be represented as having the formula of an inner oxonium or inner carbonium salt.

Professor Vieweg of the Department of Geology of Cornell University described the crystals as follows.

"The crystals of pyrogallolsulfonephthalein from distilled water are bladed. They have a green metallic surface color, and, when powdered, an orange-yellow transmission color. There is no apparent difference between the crystals from dilute hydrochloric acid and those from water. The system of crystallization could not be determined."

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[5] Sohon, *Am. Chem. J.*, 20, 257 (1898).

[6] Orndorff and Wang, This Journal, 47, 290 (1925).

Pyrogallolsulfonephthalein crystallizes best from methanol. The glistening green crystals obtained were allowed to dry in the air and analyzed.

Anal. Subs., 0.4760, 0.1927, 0.3121: loss at 130°, H_2O, 0.0566, 0.0221, 0.0360. Subs. (dry), 0.4194: $BaSO_4$, 0.2317. Calcd. for $C_{19}H_{14}O_9S + 3H_2O$: H_2O, 11.45. Found: H_2O, 11.89, 11.47, 11.53. Calcd. for $C_{19}H_{14}O_9S$: S, 7.67. Found: S, 7.59.

The substance contains three molecules of *water* of crystallization, in spite of the fact that it crystallized from methanol.

Professor Vieweg described the crystals as follows. "This substance forms rhomboid tablets, having a green surface color. The crystallization is *rhombic*. Calling the face on which the crystals lie the basal pinacoid (001), the prism angles are found, by measurement with the microscope, to be 120°. The crystals are pleochroic. Parallel to the long diagonal of the rhombus, vibrations of a greenish-yellow color are transmitted; perpendicular to this, visible light is practically completely absorbed."

Conversion into Sulfonegallein.—When pyrogallolsulfonephthalein, dried at 130°, is heated to 200° for several hours, it loses one molecule of water of constitution. The original green or greenish-brown color changes to a bright red.

Anal. Subs. (dried at 130°), 0.4929, 0.2606, 0.2851: loss at 200°, 0.0195, 0.0110, 0.0119. Calcd. for $C_{19}H_{14}O_9S$: loss of 1 H_2O, 4.31. Found: 3.96, 4.22, 4.17.

The molecule of water is split off from the two hydroxyl groups in the pyrogallol residues in the *ortho* positions to the methane carbon atom, leaving the molecule with a pyrone ring. The reverse change takes place when the sulfonegallein is allowed to stand in the air. The bright red compound takes up the molecule of water lost on heating and regains its original green color.

Anal. Subs., dried at 200°, 0.2732: gain, H_2O, 0.0143. Calcd. for $C_{19}H_{12}O_8S.H_2O$: H_2O, 4.31. Found: 4.97.

Sulfonegallein conducts itself towards most reagents in exactly the same way that pyrogallolsulfonephthalein does.

A more stable form of sulfonegallein was made as follows. A solution of 5 g. of pure pyrogallolsulfonephthalein in a small volume of 2% sodium hydroxide solution was filtered into 10 liters of cold water. Very dilute hydrochloric acid was then added until the solution was distinctly acid. A very voluminous, bright red precipitate filled the flask. Under the microscope the material was seen to be in the form of extremely fine, silky hairs. The red product was filtered off, washed, and then shaken with a liter of water, filtered, and washed again. When allowed to stand in water for any length of time, or when allowed to stand while still moist after being filtered, it changed into green pyrogallolsulfonephthalein. It was dried by pressing it between sheets of drying paper. When almost dry, it was crushed and allowed to dry in the air for a week. The analyses show that the substance is *sulfonegallein* with 3 molecules of water of crystallization.

Anal. Subs, 0.5597, 0.4947: loss at 130°, 0.0667, 0.0583. Calcd. for $C_{19}H_{12}O_8S + 3H_2O$; H_2O, 11.90. Found: H_2O, 11.92, 11.79.

Subs. (dry), 0.4820, 0.4057: $BaSO_4$, 0.2822, 0.2363. Subs. (dry), 0.1959, 0.1893: CO_2, 0.4085, 0.3959; H_2O, 0.0595, 0.0600. Calcd. for $C_{19}H_{12}O_8S$: S, 8.01; C, 56.98; H, 3.02. Found: S, 8.04, 8.00; C, 56.87, 57.04; H, 3.40, 3.55.

After loss of the 3 molecules of water at 130°, it did not lose any additional weight when heated to 200°. It does not melt below 315°.

Action of Ammonia Gas.—When exposed to dry ammonia gas until it no longer gained in weight, pyrogallolsulfonephthalein absorbed a little over 4 molecules of ammonia, and turned a bronze-blue.

Anal. Subs., 0.2768, 0.3102: Gain, 0.0483, 0.0558. Calcd. for $C_{19}H_{14}O_9S + 4NH_3$: NH_3, 14.01. Found: 14.86, 15.25.

When placed in a desiccator over concd. sulfuric acid and allowed to come to constant weight, it then contained one molecule of ammonia.

Anal. Subs., 0.2768, 0 3102: NH_3, 0.0107, 0.0135. Calcd. for $C_{19}H_{14}O_9S$ + NH_3: NH_3, 3.91. Found: 3.72, 4.17.

Sulfonegallein, dried at 130°, also absorbs between four and five molecules of ammonia, and retains one when kept in a desiccator over concd. sulfuric acid.

The red ammonium salt of pyrogallolsulfonephthalein,[7] crystallized from water has the composition represented by the formula $C_{19}H_{13}O_9SNH_4 + 2H_2O$. The monosodium salt of *pyrogallolsulfonephthalein* ($C_{19}H_{13}O_9SNa + 5H_2O$) *crystallizes* from water in needles with a reddish-brown color and slightly purplish on the surface.

When heated to 200° this salt dried, at 135°, lost another molecule of water (of constitution), leaving the monosodium salt of *sulfonegallein.*

The dizinc salt of pyrogallolsulfonephthalein ($C_{19}H_{10}O_9SZn_2 + 5H_2O$) crystallized from water had a bronze-green surface color and ground to a reddish-purple powder.

Unlike the sodium and ammonium salts of pyrogallolsulfonephthalein, the dizinc salt is only sparingly soluble in water. When heated to 200°, the dried salt loses a molecule of water of constitution, forming the dizinc salt of *sulfonegallein.*

The blue lead salt of pyrogallolsulfonephthalein ($(C_{19}H_{11}O_9S)_2Pb_3$) does not lose any weight when heated to 200°.

The reaction of pyrogallolsulfonephthalein with a soluble lead salt is very delicate and might be used as a test for either substance.

The barium salt of pyrogallolsulfonephthalein ($(C_{19}H_{13}O_9S)_2Ba + 6H_2O$) from water when dried at 130° does not lose any further weight when heated at 200°.

The normal salts of pyrogallolsulfonephthalein are red and give red solutions, while the salts formed in which some of the hydroxyl groups in the pyrogallol residues are also neutralized are blue and give blue solutions.

Action of Aniline.—When boiled with aniline, pyrogallolsulfonephthalein gives red crystals of an aniline salt of *sulfonegallein.* These lost no weight when heated to 200° and did not melt below 315°.

Anal. Subs. (dry), 0.7192, 0.6599: cc. of 0.1 *N* H_2SO_4, 14.78, 13.56. Subs. (dry), 0.5631, 0.5631: $BaSO_4$, 0 2612, 0.2590. Calcd. for $C_{19}H_{11}O_8S(C_6H_5NH_3)$: N, 2.84; S, 6.50. Found: N, 2.88, 2.88: S, 6.37, 6.32.

The reaction is quantitative. The salt is insoluble in almost all of the usual organic solvents, but is slightly soluble in water and in the alcohols.

Sulfonegallein Tetra-acetate.—When 10 g. of dry pyrogallolsulfonephthalein was boiled with 100 cc. of acetic anhydride for three hours, and half the solvent distilled, large, clear, yellow crystals were obtained. By boiling the solution in dry toluene repeatedly with bone black, the tetra-acetate was obtained as colorless, diamond-shaped crystals which melted at 218° with decomposition to a red liquid. The tetra-acetate was allowed to dry in the air for a day and analyzed.

Anal. Subs., 0.2311, 0.1858: loss at 130°, C_7H_8, 0.0233, 0.0192. Calcd. for $C_{19}H_8O_8S(C_2H_3O)_4 + C_7H_8$: toluene, 13.94. Found: 10.08, 10.33.

Subs. (dry), 0.2078, 0.1666: $BaSO_4$, 0 0850, 0.0690. Subs. (dry), 0 3348: cc. of 0.1 *N* NaOH, 23 45. Calcd. for $C_{19}H_8O_8S(C_2H_3O)_4$: S, 5.64; C_2H_3O, 30.29. Found: S, 5.62, 5.69; C_2H_3O, 30.13.

The tetra-acetate hydrolyzes slowly in the air, more rapidly in water and very readily in alkaline solution.

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[7] The details for the preparation of the salts of pyrogallolsulfonephthalein and the analytical data will be found in the dissertation of Mr. N. Fuchs in the Library of Cornell University.

That the sulfonegallein tetra-acetate contains a pyrone ring is indicated by the color changes when it is slowly saponified with sodium hydroxide solution. It shows first a green fluorescence which rapidly changes to a blue color. The acetyl groups are saponified off and the mono-, di- and tri-acetyl compounds form sodium salts that show the green fluorescence as they contain the pyrone ring. When the saponification is complete, the sulfonegallein is converted into pyrogallolsulfonephthalein by the addition of a molecule of water and hence the blue color in alkaline solution.

As was to be expected, the same tetra-acetate was obtained by boiling sulfonegallein with acetic anhydride.

Sulfonegallein Tetrabenzoate.—Five g. of pyrogallolsulfonephthalein was boiled with 25 g. of benzoyl chloride for two hours and the excess of benzoyl chloride evaporated in a water oven. The brown solid was washed with ether. Three crystallizations from dry benzene gave colorless, transparent needles which melted sharply at 235° to give a reddish liquid. When ground for analysis in an agate mortar, they became strongly electrified. The air-dried sample lost practically no weight when heated at 135°.

Anal. Subs., 0.4873, 0.4383; $BaSO_4$, 0.1368, 0.1224. Calcd. for $C_{19}H_8O_8S$-$(COC_6H_5)_4$: S, 3.93. Found: 3.86, 3.84.

Like the tetra-acetate, the tetrabenzoate of *sulfonegallein* gives a green fluorescence and then a blue color when it is slowly saponified with sodium hydroxide solution, but it is much more stable than the tetra-acetate.

Monomethyl Ether of Pyrogallolsulfonephthalein.—Four g. of *o*-sulfobenzoic acid anhydride and 4 g. of pyrogallol-1-methyl-ether[8] were heated at 135–145° for six hours. The red mass was boiled with 300 cc. of water; clusters of fine, radiating, red needles crystallized from the solution. These were recrystallized twice from methanol. The crystals had a brick-red color and crumbled to a powder when left in the air. They did not show a definite melting point, but decomposed at about 270°, turning dark green. The product was dried at 125° and analyzed.

Anal. Subs., 0.1971, 0.2054: AgI, 0.1154, 0.1127. Calcd. for $C_{19}H_{13}O_8S(OCH_3)$: CH_3O, 7.18. Found: 7.74, 7.25.

From the method used in preparing this compound, the *di*methyl ether of pyrogallolsulfonephthalein was to have been expected. But the analyses show, and the purple color in alkaline solution indicates that the substance is the *mono*methyl ether.

Sodium Salt of the Trimethyl Ether of Pyrogallolsulfonephthalein.—Twenty g. of pyrogallolsulfonephthalein was boiled in a liter of absolute methyl alcohol; 50 g. of methyl iodide, and 125 cc. of a solution of sodium methylate (made by adding 9 g. of sodium to 250 cc. of absolute methanol) were added. After the mixture had boiled for an hour, 50 g. of methyl iodide and 125 cc. of sodium methylate solution were again added. The solution turned blue and then red again. After boiling for eight hours, the red solution was concentrated to 100 cc., cooled and added to 1.5 liters of cold, anhydrous ether stirred mechanically. Twenty-one g. of material, brick-red when moist but green on drying, was filtered from the ethereal solution. This product was extracted repeatedly with boiling acetone. Most of it remained undissolved. The acetone solution yielded a few grams of crystals when it was distilled to a small volume. These were recrystallized twice from acetone and were obtained as small red crystals. They were dried at 140° and analyzed.

Anal. Subs., 0.4176: Na_2SO_4, 0.0628. Subs., 0.1346, 0.2444: AgI, 0.1905, 0.3538. Calcd. for $C_{19}H_{10}O_6SNa(OCH_3)_3$: Na, 4.77; CH_3O, 19.34. Found: Na, 4.87; OCH_3, 18.70, 19.13.

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[8] Graebe and Hess, *Ann.*, **340**, 232 (1905).

The addition of sodium hydroxide solution to an aqueous solution of this sodium salt causes the red color to change to reddish-brown, but no blue color is obtained because the presence of methoxyl groups in place of the hydroxyl groups prevents the formation of a poly sodium salt.

Trimethyl Ether.—The material left undissolved after the acetone extractions, in the experiment described above, was dissolved in a small amount of water and acidified with hydrochloric acid. From the appearance of the crystals that were precipitated, some of which were red and others orange, it seemed probable that there were at least two compounds present. The material was extracted thrice with 200cc. portions of glacial acetic acid. About half of the substance remained undissolved as a yellow powder, from which was obtained the dimethyl ether of *sulfonegallein* (see below). The acetic acid extracts gave purple-red crystals with a small amount of orange crystals. The purple-red crystals were much heavier than the orange ones, so the latter were decanted with the acetic acid from the purple-red ones. These were recrystallized twice from glacial acetic acid and then from methanol, being obtained finally as red crystals with a purplish surface tinge. The air-dried material lost very little weight when heated at 140° and did not melt when heated to 315°.

Anal. Subs. (dry), 0.1918, 0.2068: AgI, 0.2851, 0.3061. Calcd. for $C_{19}H_{11}O_6S(OCH_3)_3$: CH_3O, 20.22. Found: 19.64, 19.56.

The trimethyl ether of pyrogallolsulfonephthalein is somewhat soluble in water giving a reddish-orange solution. In dil. sodium hydroxide solution it has a light brown color. It is slightly soluble in ethanol and is insoluble in ether, acetone, benzene and chloroform.

ACTION OF AMMONIA GAS.—When the trimethyl ether was exposed to dry ammonia gas until it no longer gained in weight it absorbed about 3 molecules of ammonia.

Anal. Subs. (dry), 0.2190: gain, 0.0220. Calcd. for $C_{19}H_{11}O_6S(OCH_3)_3 + 3NH_3$: NH_3, 9.99. Found: 9.13.

A mono-ammonium salt remained when this product was allowed to stand in a desiccator over concd. sulfuric acid until it came to constant weight.

Anal. Subs., 0.2190: gain, 0.0070. Calcd. for $C_{19}H_{11}O_6S(OCH_3)_3 + NH_3$: NH_3, 3.57. Found: 3.10.

The fact that the trimethyl ether absorbs 3 molecules of ammonia is additional proof that it is a derivative of pyrogallolsulfonephthalein and not of *sulfonegallein*.

Dimethyl Ether of Sulfonegallein.—The yellow powder left undissolved after the extraction with boiling acetic acid in the above experiment was recrystallized four times from methanol. When the crystals came out of a concentrated solution they were red and came down to a sharp point at one end, but when obtained from a dilute solution they were golden-orange in color and rectangular in shape. Homogeneous samples of both forms were separated and analyzed. Neither form lost weight when heated at 130° or at 200°, and neither form melted when heated at 315°.

Anal. Subs. (red modification), 0.2588: AgI, 0.2915. Subs., 0.4719: $BaSO_4$, 0.2531. Calcd. for $C_{19}H_{10}O_6S(OCH_3)_2$: CH_3O, 14.49; S, 7.49. Found: CH_3O, 14.88; S, 7.37.

These analyses show that the red crystals are the dimethyl ether of *sulfonegallein*.

Subs. (orange modification), 0.2985: AgI, 0 3292. Subs., 0.3033: $BaSO_4$, 0.1616. Calcd. for $C_{19}H_{10}O_6S(OCH_3)_2$: CH_3O, 14.49; S, 7.49. *Found:* CH_3O, 14.57; S, 7.32.

These analyses show that the orange form is also the dimethyl ether of sulfonegallein. The two forms appear to be dimorphous modifications of the same compound. They can be converted one into the other by properly controlling the concentration of the solution. When crystallized from water they both give crystals of the orange form.

Professor Vieweg made the following report on the crystals. "The dimethyl ether has two modifications, the orange and the red. The crystals of either kind were not sufficiently large to allow measurements with the goniometer, but the crystallization could be determined with the microscope. Both varieties crystallize in the *rhombic* system. The orange crystals were rectangular tablets. They are strongly pleochroic. The red crystals have a blue metallic surface color. The pleochroism is similar to that of the orange variety, being greenish-yellow parallel to the elongation, and yellow-orange perpendicular to it. The intensity of color seems to be greater in the red crystals than in the orange, considering those of approximately the same thickness. It is interesting to note that there is a marked similarity between these two forms of the dimethyl ether, and crystals of red and yellow fluorescein, both crystallographically and with reference to the pleochroism."

Both forms have the same solubility and give the same reactions. They dissolve in dil. aqueous sodium hydroxide with development of an orange color and a pink *fluorescence.* Considering the fluorescence to be indicative of the presence of a pyrone ring, we have here further evidence that the dimethyl ethers are derivatives of *sulfonegallein* rather than of pyrogallolsulfonephthalein.

Action of Ammonia Gas on the Dimethyl Ether of Sulfonegallein.—When dry, ground samples of the red form and of the orange form of the dimethyl ether were exposed to dry ammonia gas until they no longer gained in weight; each absorbed 3 molecules of ammonia and turned a little darker in color. In the analyses below, I refers to the red form and II to the orange form.

Anal. Subs. (dry), I, 0.1353; II, 0.1033; gain, I, 0.0166; II, 0.0123. Calcd. for $C_{19}H_{10}O_6S(OCH_3)_2 + 3NH_3$: NH_3, 10.66. Found: I, 10.93; II, 10.64.

On allowing the samples saturated with ammonia to stand in a desiccator over concd. sulfuric acid until they came to constant weight it was found that a mono-ammonium salt was formed in each case.

Anal. Subs., I, 0.1353; II, 0.1033: Gain, I, 0.0053; II, 0.0042. Calcd. for $C_{19}H_{10}O_6S(OCH_3)_2 + NH_3$: NH_3, 3.83. Found: I, 3.77; II, 3.91.

Dibromo-pyrogallolsulfonephthalein.—To 8.5 g. of pyrogallolsulfonephthalein in 200 cc. of absolute ethanol was added 20 g. of bromine in 100 cc. of absolute ethanol, and the mixture boiled for six hours. The greenish, crystalline product was purified by dissolving it in boiling water and adding hydrochloric acid. The acidified solution gave glistening green crystals when it cooled. They were red when ground.

Anal. Subs., 0.2224, 0.3713; 0.2107: loss at 145°, 0.0222, 0.0371; 0.0253. Calcd. for $C_{19}H_{12}O_9SBr_2 + 4H_2O$: H_2O, 11.12. Found: 9.98, 9.99, 12.01.

Subs. (dry), 0.2002, 0.3342: AgBr, 0.1303, 0.2196. Calcd. for $C_{19}H_{12}O_9SBr_2$: Br, 27.75. Found: 27.70, 27.96.

Dibromo-pyrogallolsulfonephthalein dissolves somewhat in water with development of a purplish-red color and is slightly soluble in the alcohols, but is insoluble in most of the organic solvents. Sodium hydroxide solution dissolves it very readily, producing in very dilute solutions of the alkali a deep red color due to the formation of a monosodium salt, and in an excess of the alkali a deep blue color caused by the formation of a polysodium salt, but the solutions show no fluorescence. It does not melt when heated to 315°.

After being dried at 145°, the dibromo-pyrogallolsulfonephthalein lost another molecule of water (of constitution) when heated to 200°, forming *dibromo-sulfonegallein.*

Anal. Subs. (dry), 0.3113, 0.1672: loss at 200°, 0.0092, 0.0045. Calcd. for $C_{19}H_{12}O_9SBr_2$: loss of $1H_2O$, 3.13. Found. 2.96, 2.69.

Action of Ammonia Gas.—When dry dibromo-pyrogallolsulfonephthalein was exposed to dry ammonia gas until it no longer gained in weight, it absorbed almost 6 molecules of ammonia, and became dark red.

Anal. Subs. (dry), 0.2976: gain, 0.0498. Calcd. for $C_{19}H_{12}O_9SBr_2 + 6NH_3$: NH_3, 15.07. Found: 14.33.

On allowing the dibromo-pyrogallolsulfonephthalein saturated with ammonia to stand in a desiccator over concd. sulfuric acid until it came to constant weight, it was found that the substance retained almost 3 molecules of ammonia.

Anal. Subs., 0.2976: gain, 0.0228. Calcd. for $C_{19}H_{12}O_9SBr_2 + 3NH_3$: NH_3, 8.15. Found: 7.12.

When *dibromo-sulfonegallein* was exposed to dry ammonia gas it absorbed 5 molecules, and retained 3 of them in a desiccator over sulfuric acid.

AMMONIUM SALT.—This salt was made in the same way as the ammonium salt of pyrogallolsulfonephthalein. The needle-shaped crystals were bronze-green by reflected light and were ground to a reddish-brown powder.

Dibromo-sulfonegallein Tetrabenzoate.—Five g. of dry dibromopyrogallolsulfonephthalein was boiled with 35 g. of benzoyl chloride, evaporated in a water-oven and the last traces of benzoyl chloride removed by washing the dark solid remaining with a little ether. The product was purified by boiling it with benzene, using bone black. After three recrystallizations from benzene, it was obtained as colorless, needle-like crystals, which melted to a reddish liquid at 269–270°. The air-dried crystals lost no weight when heated at 120°.

Anal. Subs., 0.3806, 0.2994: AgBr, 0.1459, 0.1135. Calcd. for $C_{19}H_6O_8SBr_2(COC_6H_5)_4$: Br, 16.41. Found: 16.31, 16.13.

*Di*bromo-sulfonegallein tetrabenzoate is very soluble in benzene and in chloroform, and is only slightly soluble in ether. It is practically insoluble in water, but hydrolyzes slowly in it. It shows a green fluorescence in dil. sodium hydroxide solution, but this soon changes to the blue color that dibromo-pyrogallolsulfonephthalein has in alkaline solution, showing that saponification has taken place.

Pyrogallolsulfonephthal*in*.—A suspension of 5 g. of pyrogallolsulfonephthalein and 10 g. of zinc dust in 100 cc. of water was boiled for an hour. The mixture first became blue due to the formation of the zinc salt of pyrogallolsulfonephthalein, but this was soon reduced to the zinc salt of pyrogallolsulfonephthal*in*, leaving the solution with a faint orange-brown color. The excess of zinc dust was filtered off and 400 cc. of concd. hydrochloric acid added. Lustrous, transparent, silvery-brown crystals began to form very rapidly. They were again crystallized by the addition of a large excess of concd. hydrochloric acid. After five such recrystallizations, the crystals were almost colorless. They were dried in a vacuum desiccator over concd. sulfuric acid and ground sodium hydroxide and analyzed.

Anal. Subs., 0.3485, 0.4065: loss at 120°, 0.0159, 0.0149. Calcd. for $C_{19}H_{16}O_9S + H_2O$: H_2O, 4.11. Found: 4.56, 3.67.

Subs. (dry), 0.3326, 0.3916: $BaSO_4$, 0.1844, 0.2169. Calcd. for $C_{19}H_{16}O_9S$: S, 7.63. Found: 7.62, 7.61.

When heated in a melting-point tube, it contracts to a dark red tar at 146–147° but it does not fuse to the glass until the temperature reaches 170°. At about 226° it foams and decomposes. Pyrogallolsulfonephthal*in* is readily oxidized to pyrogallolsulfonephthalein. It turns red even when kept in a tightly corked vial. It dissolves in dil. sodium hydroxide solution without development of color, but when the solution is allowed to stand in the air, oxidation takes place and the solution turns blue, due to the formation of the polysodium salt of pyrogallolsulfonephthalein. Pyrogallolsulfonephthal*in* is very soluble in methanol, ethanol, ether, acetone, glacial acetic acid and water but is insoluble in chloroform and carbon tetrachloride.

ZINC SALT.—A suspension of 5 g. of pyrogallolsulfonephthalein and 10 g. of zinc dust in 100 cc. of water was boiled for an hour. The excess of zinc was filtered off and the filtrate concentrated to 25 cc. in the presence of a small piece of zinc. To prevent oxidation of the solution it was cooled in carbon dioxide and stoppered tightly. Crystals with a slight pink tint formed. These, with the zinc that had been added, were filtered off rapidly and the crystals then dissolved in a small volume of hot water. This solution was filtered from the zinc directly into a large test-tube that was then tightly corked and set aside for crystallization to take place. The crystals obtained in this way were colorless except for a slight pink tint. They seemed to lose moisture slowly when left in the air, and crumbled to a powder. Analyses showed the crystals to be the normal zinc salt of pyrogallolsulfonephthal*in* with 2 molecules of water of crystallization.

Anal. Subs., 0.5021, 0.5847: loss at 125°, 0.0201, 0.0245. Calcd. for $(C_{19}H_{15}O_9S)_2Zn + 2H_2O$: H_2O, 3.83. Found: 4.00, 4.19.

Subs. (dry), 0.5188, 0 4975, 0.4820: $ZnSO_4$, 0.0897, 0.0870, 0.0838. Subs. (dry), 0.5602, 0.5265: $BaSO_4$, 0.2784, 0 2603. Calcd. for $(C_{19}H_{15}O_9S)_2Zn$: Zn, 7.23; S, 7.09. Found: Zn, 7.00, 7.08, 7.04; S, 6.83, 6.79.

The zinc salt does not oxidize as readily as pyrogallolsulfonephthal*in*, although it gives the blue zinc salt of pyrogallolsulfonephthalein when air is passed into an aqueous solution of it.

After being dried at 125°, the zinc salt of pyrogallolsulfonephthal*in* loses 2 molecules of water of constitution when heated at 200°, forming the zinc salt of the *sulfonegallin*.

Anal. Subs. (dried at 125°), 0.4820: loss at 200°, 0.0185. Calcd. for $(C_{19}H_{15}O_9S)_2Zn$: loss of $2H_2O$, 3.99. Found: 3.84.

Summary

1. 2,3,4-Trihydroxybenzoyl-benzene-*o*-sulfonic acid and its tribenzoate have been isolated. 2,3,4-Trihydroxybenzoyl-benzene-*o*-sulfonic acid is an intermediate product in the formation of pyrogallolsulfonephthalein. When heated alone or with pyrogallol, it gives pyrogallolsulfonephthalein.

2. Methods for the preparation of pure, crystallized pyrogallolsulfonephthalein ($C_{19}H_{14}O_9S$) have been given. It is best made from the anhydride of *o*-sulfobenzoic acid and pyrogallol. Pyrogallolsulfonephthalein does not fluoresce in alkaline solution.

3. Sulfonegallein ($C_{19}H_{12}O_8S$) has been made by heating pyrogallolsulfonephthalein at 200°, and by acidifying a dilute alkaline solution of pyrogallolsulfonephthalein *in the cold*. Sulfonegallein reverts to pyrogallolsulfonephthalein in the presence of water. When pyrogallolsulfonephthalein reacts with certain reagents derivatives of sulfonegallein result.

4. Pyrogallolsulfonephthalein, as well as sulfonegallein, reacts as a tautomeric substance, giving *colored* quinoid and *colorless* lactoid derivatives. Pyrogallolsulfonephthalein and its salts, and sulfonegallein and its salts are colored compounds having the quinoid structure. The colorless tetra-acetate and tetrabenzoate of *sulfonegallein* are derivatives of the lactoid form.

5. The *colored* monomethyl and trimethyl ethers of pyrogallolsulfonephthalein and the dimethyl ether of *sulfonegallein*, as well as their colored ammonium salts, have been made and have the quinoid structure.

6. Dibromo-pyrogallolsulfonephthalein is a tautomeric substance, having for itself and its ammonium salt the colored quinoid structure, and forming the colorless, dibromo-*sulfonegallein* tetrabenzoate, which has the lactoid structure.

7. Pyrogallolsulfonephthal*in* and its zinc salt have been made. They are colorless. Pyrogallolsulfonephthal*in* is very readily oxidized by the air to pyrogallolsulfonephthalein.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL RESEARCH, PARKE, DAVIS AND COMPANY, No. 37]

RING CLOSURE IN CHLORO-ALKYL PHENYLCARBAZATES. SIX- AND SEVEN-MEMBERED HYDRAZOLACTONES

BY ARTHUR W. DOX

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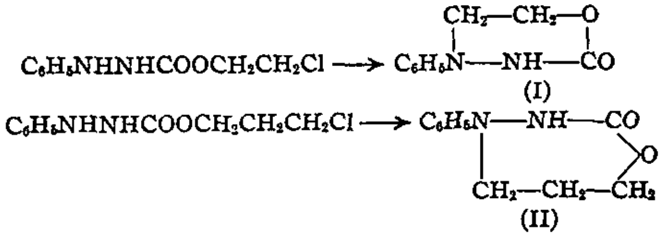
The tendency of cyclic compounds to form when halogen and hydrogen are removed by simple treatment with alkali from the terminal atoms of a five- or six-membered open chain has made possible the synthesis of numerous new heterocyclic structures. In a previous paper[1] this reaction was applied to the synthesis of 1,3-oxazine derivatives from γ-chloropropyl carbanilates. It was shown that such ring closure took place only when the amide grouping was stabilized by the introduction of phenyl; otherwise, a decomposition occurred with formation of alkali cyanate.

A similar reaction should occur with chloro-alkyl phenylcarbazates, which are analogous to the carbanilates except for the presence of an additional NH group, and the ring closure should yield cyclic derivatives with two nitrogens and one oxygen as the hetero elements.

The two esters studied were the β-chloro-ethyl and the γ-chloropropyl. Assuming that the terminal NH of the phenylcarbazic acid group furnishes the hydrogen which is split out as hydrogen chloride, the resulting cyclic derivatives should contain six and seven members, respectively.



(I)

(II)

Such heterocycles containing an oxygen in the ring adjacent to a carbonyl may also be regarded as lactones and should be hydrolyzed easily by aqueous alkali. Hence, the yield is better when sodium ethoxide in absolute

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[1] Dox and Yoder, THIS JOURNAL, 45, 723 (1923).

alcohol is used as the condensing agent, and only the calculated amount employed. A further advantage of this treatment is the greater solubility of the esters in alcohol than in water. The condensation product is, as a rule, less soluble than the ester, and often crystallizes without evaporation when a minimum amount of solvent is used.

Experimental Part

β-Chloro-ethyl Phenylcarbazate.—Fifty g. of phenylhydrazine was dissolved in 50 g. of pyridine and the solution diluted with 200 cc. of water. The flask was then immersed in cold water and the solution stirred continuously during the gradual addition of 66 g. of β-chloro-ethyl chlorocarbonate from a dropping funnel. The reaction was accompanied by a moderate evolution of heat. A red oil separated and soon solidified into crystalline lumps. These were filtered off, broken up and thoroughly washed with water until only a faint odor of pyridine remained. The crude product weighed 73.6 g. Recrystallization from benzene removed the color completely and the final product was obtained in white, needle-shaped crystals melting at 89°. It is practically insoluble in water, but soluble in the usual organic solvents.

Anal. Subs , 0.1612: AgCl, 0.1058. Calcd. for $C_9H_{11}O_2N_2Cl$: Cl, 16.55. Found: 16 23.

2-Keto-4-phenyl-tetrahydro-1,3,4-oxidazine (lactone of β-hydroxyethylphenylcarbazic acid).—A solution containing 25 g. of β-chloro-ethyl phenylcarbazate in 200 cc. of absolute alcohol was treated with the exact equivalent of sodium ethoxide in absolute alcohol (73.3 cc. of 1.59 *N* solution). A slight evolution of heat occurred and an almost immediate separation of sodium chloride. Within five minutes the reaction mass had become neutral to litmus, without the application of heat. The sodium chloride was filtered off and the yellow filtrate carefully evaporated. Yellow crystals were obtained, together with some oily impurity which was removed by absorption on a porcelain tile. Recrystallization from benzene gave a pure white product consisting of scaly crystals melting at 120°. The yield of pure substance was 9.89 g. It is sparingly soluble in hot water from which it crystallizes in flat prisms on cooling, but more readily soluble in alcohol, benzene and ether.

Anal. Subs., 0 2252: CO_2, 0.5035; H_2O, 0.1185. Subs , 0.1486. N_2, 22.0 cc. (25°, 729 mm.). Calcd. for $C_9H_{10}O_2N_2$: C, 60.68; H, 5.62; N, 15.73. Found: C, 60 98; H, 5.85; N, 15.82.

γ-Chloropropyl Phenylcarbazate.—This was obtained from phenylhydrazine and γ-chloropropyl chlorocarbonate in dil. pyridine in exactly the same manner as that described above for the chloro-ethyl ester. The product separated at first as an oil which solidified when cooled in an ice-bath. Recrystallization from benzene gave white, scaly crystals melting at 72°. From 36 g. of phenylhydrazine and 52 g. of chlorocarbonate the yield was 44.2 g. of pure product.

Anal. Subs., 0.2042: AgCl, 0.1269. Calcd. for $C_{10}H_{13}O_2N_2Cl$: Cl, 15.54. Found: 15.37.

Lactone of γ-hydroxypropyl-phenylcarbazic acid.—Twenty g. of the ester just described was dissolved in 100 cc. of absolute alcohol and the solution treated with the exact equivalent of sodium ethoxide in absolute alcohol (42.0 cc. of 3.92 *N* solution). Sodium chloride began to separate immediately, and in a few minutes the mixture had become neutral. The filtrate began to deposit crystals of the lactone before evaporation of the solvent. After recrystallizing from benzene the yield was 7 53 g. of white, scaly crystals; m. p. 146°. The substance is somewhat less soluble in alcohol than the analogous oxdiazone, but is readily soluble in benzene and ether. The nomenclature of ring systems has not yet been extended to include seven-membered heterocycles, but this type might provisionally be designated a homo-oxdiazine.

Anal. Subs., 0.2028: CO_2, 0.4699; H_2O, 0.1177. Subs., 0.1704: N_2, 22.8 cc. (25°, 740 mm.). Calcd. for $C_{10}H_{12}O_2N_2$: C, 62.50; H, 6.25; N, 14.58. Found: C, 63.19; H, 6.45; N, 14.53.

Attempts to alkylate the two hydrazolactones described above were unsuccessful. When refluxed in alcoholic solution with sodium ethoxide and ethyl bromide, the mixture eventually became neutral, but the lactones were recovered for the most part unchanged. Neutrality resulted apparently by removal of hydrogen bromide from the ethyl bromide to form ethylene or ethyl ether as indicated by the separation of sodium bromide, or possibly in part by formation of the sodium salt of the acid corresponding to the lactone. The free acid, however, could not be obtained in sufficient yield or purity for identification. This failure to form alkyl derivatives supports the assumption that the ring closure occurred as indicated in Formulas I and II, since the hydrogen to be replaced is present in an amide grouping. On the other hand, the isomeric five- and six-membered rings with aniline groupings as side chains would be expected to react without difficulty.

More conclusive proof of the structure indicated by Formula II was obtained by hydrolysis and reduction. One g. of the seven-membered lactone was treated with 20 cc. of hydrochloric acid, in which it dissolved completely, and 2 g. of tin foil. After the tin had dissolved, the mixture was diluted with water, made strongly alkaline with sodium hydroxide and distilled to half its volume. The distillate was slightly alkaline to litmus (ammonia), but showed no cloudiness, and hence could not have contained any significant amount of aniline. On the other hand, the residue contained oily drops possessing a faintly basic odor. This non-volatile amine was extracted with ether and the solvent evaporated, leaving 0.5 g. of a yellow basic oil which was readily soluble in hydrochloric acid. When treated with sodium hydroxide and benzene sulfochloride, this oil yielded a red oil which was insoluble in both acid and alkali. The condensation product could not be solidified in a freezing mixture. The formation of a secondary amine thus establishes the fact that ring closure has occurred with substitution of the end nitrogen of the phenylcarbazic acid. The isomeric six-membered oxazine should yield aniline when subjected to this treatment.

The sulfur analog of Formula I, with two sulfurs in place of the two oxygens, has been described by Busch[2] and designated phenylpentathiodiazthine. The synthesis was, in this case, by an altogether different method, and consisted in the condensation of potassium phenylthiocarbazate with ethylene bromide. The product thus obtained differed from

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[2] Busch, *Ber.*, **27**, 2516 (1894).

both of the above lactones in that the alcoholic solution gave a blue violet color with ferric chloride, whereas the lactones gave no color whatever.

In order to test further the applicability of pyridine as a condensing agent in the reaction between hydrazines and alkyl chlorocarbonates, the butyl esters of phenylcarbazic acid and hydrazodicarboxylic acid were prepared.

***n*-Butyl Phenylcarbazate.**—A solution of 3.1 g. of phenylhydrazine and 3.1 g. of pyridine in 15 cc. of water was treated with 3.9 g. of *n*-butyl chlorocarbonate. A yellow oil separated and solidified on cooling. After being thoroughly washed with water and recrystallized from benzene, the product was obtained in white, scaly crystals melting at 70°.

Anal. Subs., 0.1973: N_2, 25.2 cc. (25°, 745 mm.). Calcd. for $C_{11}H_{16}O_2N_2$: N, 13.46. Found: 13.95.

***n*-Butyl Bicarbamate.**—A solution of 34 g. of hydrazine hydrate (40%) and 25 g. of pyridine in 100 cc. of water was treated with 18.5 g. of butyl chlorocarbonate. The oil which separated was thoroughly washed by shaking with water and dil. acetic acid, and allowed to stand in an ice box overnight. A mass of scaly crystals was thus obtained which after recrystallization from benzene melted at 47°.

Anal. Subs., 0.1600: CO_2, 0.3036; H_2O, 0.1314. Subs., 0.2087: N_2, 22.9 cc. (24°, 753 mm.). Calcd. for $C_{10}H_{20}O_4N_2$: C, 51.73; H, 8.62; N, 12.07. Found: C, 51.74; H, 8.92; N, 12.08.

The two cyclic derivatives, I and II, representing as they do new types of ring structures, were of interest as possible pharmacological agents. Preliminary tests, however, failed to reveal any noteworthy physiological action. When administered orally in 1g. doses to normal dogs of about 10 kg. weight, no marked symptoms were observed, either of gastric or intestinal disturbance, or of narcotic or toxic action. The hydrazine grouping present might, however, lead one to expect a certain degree of antipyretic action, and it is planned to perform a suitable test of this effect in the near future.

Summary

Heterocycles containing two nitrogens and one oxygen, and representing six- and seven-membered ring structures, respectively, were prepared by removal of hydrogen chloride from the β-chloro-ethyl and the γ-chloropropyl esters of phenylcarbazic acid. These hydrazolactones represent new types, the first of which may be designated a 1,3,4-oxdiazine, but for the second our present system of cyclic nomenclature is inadequate. Provisionally, the latter may be designated a homo-1,3,4-oxdiazine. No noteworthy pharmacological action was observed when these derivatives were administered orally in 1g. doses to normal dogs.

DETROIT, MICHIGAN

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY OF MICHIGAN STATE COLLEGE]

THE EFFECT OF UNSATURATION ON THE ACTIVITY OF ALCOHOLIC HYDROXYL. I. ACTION OF ALLYL ALCOHOL ON BENZENE IN THE PRESENCE OF ALUMINUM CHLORIDE

BY R. C. HUSTON AND D. D. SAGER

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Continuing our studies on the condensation of aromatic alcohols and aromatic hydrocarbons in the presence of aluminum chloride, an attempt was made to condense phenylethyl alcohol and benzene by means of aluminum chloride. The results were negative in so far as the production of diphenylethane was concerned. Attempts to prepare symmetrical diphenylpropane from phenylpropyl alcohol and benzene were also unsuccessful.

Our earlier work had shown that both methylphenylcarbinol and ethylphenylcarbinol readily condense with benzene, and the failure of their isomers to respond under similar treatment was regarded as significant. *Of the aromatic alcohols studied, only those in which the hydroxyl is on the carbon atom adjacent to the ring were found to react.*

The method was next applied to a number of aliphatic alcohols; methyl, ethyl, propyl, secondary propyl, *n*-butyl, *iso*butyl and *iso*-amyl alcohols were included. In no case was there evidence of the formation of the corresponding alkyl benzene.

This lack of reactivity of the simple aliphatic alcohols was expected. Goldschmidt[1] was able to effect condensation in the presence of zinc chloride only at relatively high temperatures, while Brochet and Borlinger[2] obtained a small yield of the alkyl benzene by heating the alcohol and benzene for several hours at 175–200° in the presence of an excess of sulfuric acid.

From the results it is apparent that the activity of the hydroxyl group is greatly enhanced when it is attached to a carbon atom which is in turn attached to a carbon of the benzene ring, and the question naturally arose as to what effect unsaturation, other than that of the benzene ring, would have upon the activity of the hydroxyl group.

This paper describes experiments in which a simple unsaturated aliphatic alcohol, allyl alcohol was mixed with an excess (5 molecular equivalent) of benzene and treated with aluminum chloride (0.5 equivalent) at room temperature. The principal product of the reaction was allyl benzene: $CH_2{=}CH{-}CH_2OH + C_6H_6 \longrightarrow CH_2{=}CHCH_2C_6H_5 + H_2O$. It was identified by conversion into propenylbenzene, by boiling with alcoholic

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[1] Goldschmidt, *Ber.*, **15**, 1066 (1882).

[2] Brochet and Borlinger, *Compt. rend.*, **117**, 235 (1893).

potassium hydroxide.[3] The yield was smaller than that obtained in those condensations where aromatic alcohols were used, 16% as compared with 67% for benzyl alcohol.

From the higher-boiling portion of the reaction product there was isolated by repeated fractionation under reduced pressure a considerable amount of chloropropylbenzene. This was probably the result of addition of hydrochloric acid to allylbenzene under the catalytic influence of aluminum chloride: $C_6H_5CH_2CH{=}CH_2 + HCl \longrightarrow C_6H_5CH_2CHClCH_3$. The formation of this compound is in part responsible for the low yield of allylbenzene.

The next higher fraction was freed from halogen by boiling in ether solution with sodium and was refractionated. After purification it came over at 277–280° (745 mm.). It has the properties of a saturated hydrocarbon and is probably 1,2-diphenylpropane. Silva[4] obtained this compound when he attempted to prepare allylbenzene from allylchloride and benzene by the Friedel and Crafts reaction. He attributed its formation to the intermediate formation of 1,2-dichloropropane from allyl chloride or of β-chloropropylbenzene from allylbenzene. The isolation of β-chloropropylbenzene from our reaction product would indicate the correctness of his second hypothesis. One experiment with a small amount of material indicated the formation of 1,2-diphenylpropane directly from allylbenzene, benzene and aluminum chloride.

The literature gives no definite data on the preparation and properties of β,γ-dibromopropylbenzene. This was prepared by treating pure allylbenzene in chloroform solution with the calculated amount of bromine.

Discussion

In the compounds studied, there appears to be a very definite relationship between reactivity of the hydroxyl group and the state of saturation of the alpha carbon atom. *Only those compounds in which the alpha carbon is a member of the benzene ring or is double bonded show appreciable reactivity.*

In the aromatic alcohols the difference in activity of the phenylalkylcarbinols and those isomers in which the hydroxyl is on the second or third carbon atom from the ring, is also apparent in their behavior toward heat. When heated under atmospheric pressure to their boiling points, phenylmethylcarbinol and phenylethylcarbinol lose water to form the corresponding unsaturated hydrocarbons, while phenylethyl alcohol and phenylpropyl alcohol may be distilled without decomposition at atmospheric pressure.

It is also well known that benzyl alcohol, benzohydrol, phenylmethylcarbinol and phenylethylcarbinol, react more readily with halogen acid to

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[3] Tiffeneau, *Compt. rend*, 139, 1482 (1904).

[4] Silva, *Compt. rend.*, 89, 606 (1879).

form halogen derivatives, than do those compounds in which the hydroxyl is more distant from the phenyl group.

A certain parallelism is evident between the activity of the hydroxyl group and halogen. Claisen[4a] has explained the formation in benzene or toluene solution, of different amounts of *o*-allyl- or *o*-benzylphenol (and the lack of formation of *o*-alkyl phenol) from the corresponding halide, on the basis of a loosening effect of the double bond or benzene ring on the bond between carbon and halogen. Conant and Kirner[5] found a sharp decrease in reactivity of the halogen toward potassium iodide in passing from benzyl chloride to phenylethyl chloride and the higher homologs. An especially interesting comparison is found in the reactivity of propyl halide, allyl halide and benzyl halide toward potassium iodide,[6] sodium thiosulfate[7] and pyridine.[8] With all three reagents the allyl halide has a reactivity greater than the propyl halide, and less than the benzyl halide. Our work has shown the same relative order of reactivity in the alcohols when condensed with benzene in the presence of aluminum chloride.

Experimental Part

Allyl Alcohol, Benzene and Aluminum Chloride.—Eighty-seven g. of allyl alcohol, b. p. 95–97°, was dissolved in 585 g. of benzene and the solution stirred constantly during the addition of 99 g. of aluminum chloride. The addition of the chloride took, in general, from two to three hours, during which time the temperature was maintained at 20–25°. Hydrogen chloride was copiously evolved. The stirring was continued for about eight hours, while the mixture gradually became dark reddish-brown. The next morning it was decomposed with ice and dil. hydrochloric acid. The benzene layer was separated and the aqueous portion extracted thrice with ether. The ether was distilled and the residue added to the benzene portion. This was fractionated with a 20cm. column; 510 g. of benzene and 30 g. of allyl alcohol were recovered from those portions which came over below 105°. The residue weighed 28 g. This was combined with the products of two other runs, and fractionated eight times. The fractions obtained were as follows: 105–165° 45 g.; 85–105 (18 mm.) 10 g.; 105–135 (18 mm.) 1 g.; 135–170 (18 mm.) 14.5 g.; tarry residue 14 g. Practically all of the fraction boiling at 105–165° (746 mm.) proved to be allyl benzene (b. p., 157–159°).

In order to verify the identification, 4 g. of allyl benzene was heated on the water-bath with 8 g. of potassium hydroxide in 80 cc. of 95% alcohol for three hours. Most of the alcohol was then distilled and 250 cc. of water added. After the solution was neutralized with hydrochloric acid, it was extracted with ether. The ether was distilled and the propenylbenzene treated in chloroform solution with 2 cc. of bromine. After two crystallizations from alcohol the α,β-dibromopropylbenzene melted sharply at 66–66.5°.[9]

The 85–105 (18 mm.) fraction came over after repeated distillation at 90.5 to

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[4a] Claisen, *Ann.*, **442**, 216, 213 (1925).

[5] Conant and Kirner, THIS JOURNAL, **46**, 232 (1924).

[6] Conant, Kirner and Hussey, *ibid.*, **47**, 476 (1925).

[7] Slator, *J. Chem. Soc.*, **85**, 1286 (1904); **87**, 481 (1905); **95**, 93 (1909).

[8] Clarke, *ibid.*, **97**, 416 (1910); **99**, 1927 (1911); **101**, 1788 (1912); **103**, 1689 (1913).

[9] Hell and Bauer, *Ber.*, **36**, 206 (1903).

92.5° (18 mm.). When distilled under atmospheric pressure it had the correct boiling point for β-chloropropylbenzene,[10] 205–207°. A determination of chlorine (Carius) gave 21.75%. When boiled with dil. nitric acid (10%) it gave *p*-nitrobenzoic acid (m. p., 237–238°) the methyl ester of which melted at 96°. Oxidation with potassium permanganate gave benzoic acid.

The fraction boiling at 135–170° (18 mm.) did not give a sharp boiling point after ten distillations. A Carius determination for chlorine gave 5.53%. The entire fraction was dissolved in 50 cc. of ether, the solution treated with 1 g. of finely chipped sodium and refluxed on a water-bath for four hours. The mixture was filtered, the ether evaporated and the residue fractionated. After three distillations 6.5 g. came over at 277–280° (745 mm.). This fraction was entirely free from halogen. Its properties were those of a saturated hydrocarbon. It is probably 1,2-diphenylpropane,[3] C_6H_5-$CHCH(C_6H_5)CH_3$.

Allylbenzene, Benzene and Aluminum Chloride.—Eleven g. of allylbenzene and 34.5 g. of benzene were treated with 6 g. of aluminum chloride under the usual conditions. The temperature was kept below 25°. The mixture turned dark brown and hydrogen chloride was evolved. Decomposition, extraction and distillation were effected as in the preceding experiment. The following fractions were obtained: 105–270°, 2 g.; 270–285° (mostly 276–280°), 4.5 g.; 285–320°, 1 g.; residue, 6 g.

β,γ-Dibromopropylbenzene.—Twenty g. of allylbenzene dissolved in 125 cc. of chloroform was treated with bromine in 0.25cc. portions until 8.75 cc. (28 g.) had been added, when the bromine color ceased to disappear (calculated amount, 27.12 g.). The chloroform was allowed to evaporate and the residue distilled under reduced pressure. After two fractionations, 39 g. of β,γ-dibromopropylbenzene distilled at 114–115° (5 mm.). It boils under atmospheric pressure at 242–244° with considerable decomposition; d_4^{20}, 1.62.[11]

Calcd. for $C_9H_{10}Br_2$: Br, 57.51. Found: 57.52, 57.70.

Effect of Aluminum Chloride on Mixtures of Benzene with Phenylethyl Alcohol, Phenylpropyl Alcohol and Saturated Aliphatic Alcohols

The conditions in each case were as nearly the same as those used with allyl alcohol and the aromatic alcohols as possible. Two molecular equivalents of the alcohol were dissolved in ten equivalents of benzene and treated with one equivalent of aluminum chloride. The temperature was kept at 20–25°. Hydrogen chloride was slowly evolved, but there was no evidence of vigorous reaction. After standing overnight the mixture was decomposed, extracted and distilled as usual.

In the following table there is recorded the amount of distillate which came over in the second distillation within a range of 10° on either side of the boiling point of the expected alkyl benzene.

Alcohol	methyl	ethyl	propyl	*iso*propyl	butyl	*iso*butyl	*iso*-amyl	phenyl-ethyl	phenyl-propyl
Temp., °C.	103–122	126–146	149–169	143–163	170–190	161–181	180–204	274–294	280–300
Distillate, g.	0.30	0.10	0.15	0.10	0.00	0.00	0.00	0.15	0.20

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[10] Errera, *Gazz. chim. ital.*, 16, 320 (1886); *J. Chem. Soc.*, 52, 35 (1887).

[11] Luib, *Ann.*, 283, 304 (1894).

Summary

1. Of the alcoholic derivatives of aromatic hydrocarbons, only those in which the hydroxyl is on the carbon atom adjacent to the ring condense with benzene in the presence of aluminum chloride.

2. The saturated aliphatic alcohols up to and including amyl alcohol do not react with benzene in the presence of aluminum chloride to form alkylbenzenes.

3. Allyl alcohol condenses with benzene to give a fair yield (16%) of allylbenzene: $CH_2{=}CHCH_2OH + C_6H_6 \longrightarrow CH_2{=}CHCH_2C_6H_5 + H_2O$.

4. Unsaturation on the carbon atom, adjacent to the alcoholic group, increases the reactivity of the hydroxyl toward the dehydrating effect of aluminum chloride.

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[Contribution from the Chemistry Department of the University of Bristol]

THE CONSTITUTION OF CATECHIN. IX. SOME NEW DISINTEGRATION PRODUCTS OF ACACATECHIN

By M. Nierenstein

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Various formulas have been suggested by Freudenberg and his collaborators for catechin including Formula I, which was considered untenable[1] in 1924, but is now regarded as the correct formula for epicatechin[2] and catechin[3] respectively, since cyanidin chloride (II) may be reduced to epicatechin. It is beyond the limits of the present communication to discuss the validity of this formula of cyanidin chloride and reference must be made to (1) Willstätter and Mallison,[4] from whom it will become evident that the formula of cyanidin chloride is based on very slender evidence and (2) to Willstätter, Zechmeister and Kindler[5] as well as to the work of Pratt and Robinson[6] from which it will also become evident that so far no convincing synthesis of cyanidin chloride has been accomplished by these workers since the synthetic products obtained by them have been shown only to be similar to but not convincingly identical with cyanidin chloride. As the matter stands at present there is as much evidence in favor of Formula IV for cyanidin chloride as for Formula II[7] and the production of catechin from cyanidin chloride may well be quoted in favor of the author's formula (V) for acacatechin.

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[1] Freudenberg, Orthner and Fikentscher, *Ann.*, **436**, 290 (1924).

[2] Freudenberg, Fikentscher, Harder and Schmidt, *Ann.*, **444**, 135 (1925).

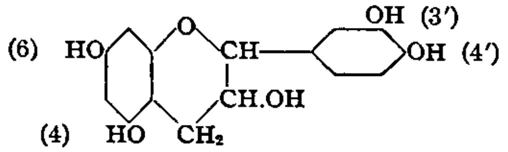
[3] Freudenberg, Carrara and Cohn, *Ann.*, **446**, 87 (1925).

[4] Willstätter and Mallison, *Ann.*, **408**, 24 (1915).

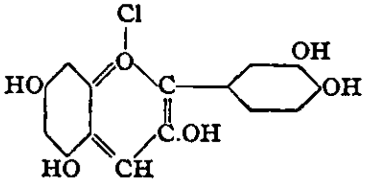
[5] Willstätter, Zechmeister and Kindler, *Ber.*, **57**, 1944 (1924).

[6] Pratt and Robinson, *J. Chem. Soc.*, **127**, 172 (1925).

[7] Compare Ref. 4, p. 23.



I



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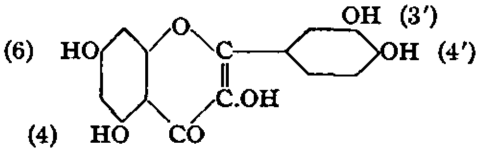

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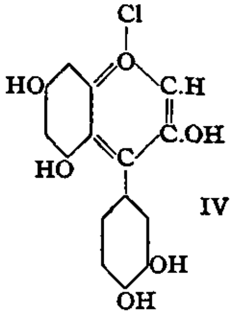

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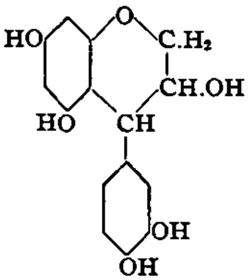

V

In further support of their Formula I for catechin Freudenberg and his collaborators[8] also state that the pentamethylether of Substance II, which had been prepared according to the method of Pratt and Robinson,[9] may be reduced to a substance melting at 114–116° and that this reduction product is in every respect identical with pentamethyl-epicatechin. Experience which has accumulated in this Laboratory during the last fourteen years makes it hard to understand these results, as only the following two *optically inactive* pentamethylethers have so far been met by us: pentamethyl-acacatechin, m. p. 107°, which is described in the present communication and pentamethyl-iso-acacatechin, m. p. 127°, previously communicated.[10]

In view of these considerations the author's opinion as to the constitution of acacatechin, which is supported by a series of observations recorded in the present communication remains unaltered.

In Part VII of this series[11] it was mentioned that all attempts to reduce quercetin (III) to acacatechin have only yielded negative results and it was therefore thought desirable to attempt the oxidation of acacatechin as on the basis of the Freudenberg formula for catechin (I) the production of quercetin might be anticipated. The scheme adopted was the following:

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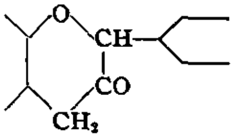
[8] Ref. 2, p. 142.

[9] Ref. 6, p. 171.

[10] Nierenstein, *Ber.*, 56, 1879 (1923).

[11] Nierenstein, THIS JOURNAL, 46, 2794 (1924).

4,6,3′,4′-tetramethyl-acacatechin was to be oxidized to the ketone (VI) from which the isonitroso derivative (VII), which would yield 4,6,3′,4′-tetramethyl-quercetin on hydrolysis, was to be prepared.



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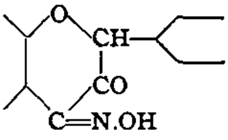
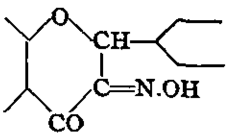


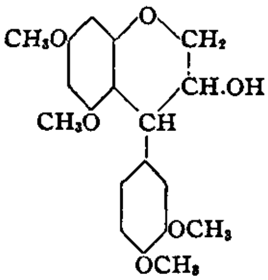
VII



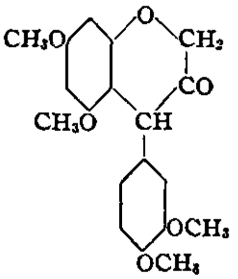
VIII

No difficulties were met in the preparation of the ketone and the isonitroso derivative, but no 4,6,3′,4′-tetramethyl-quercetin was obtained on hydrolysis. This is not consistent with Formula I for catechin, especially if one considers that the isomeric isonitroso derivative (VIII) is known to yield 4,6,3′,4′-tetramethyl-quercetin.[12]

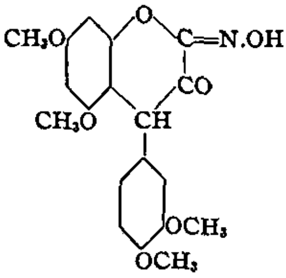
As will be realized, the reaction proceeds according to the Formulas IX, X, XI, XII and XIII, with the result that not tetramethyl-quercetin, but 2-hydroxy-4,6,3′,4′-tetramethoxy-3-phenylcoumarin (XIII) is produced. During these reactions both the α-diketonic (XII) and the enolic (XIII) forms can be isolated, which is not the case in the flavonol syntheses of Kostanecki. The α-diketone (XII) is, however, best prepared by the oxidation of the ketone (X) with neutral permanganate in acetone solution.



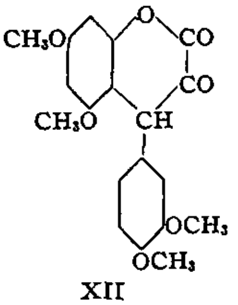
IX



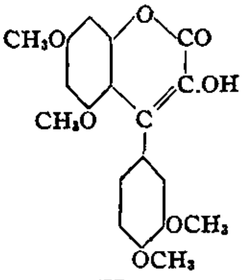
X



XI



XII



XIII

The constitution of 2-hydroxy-4,6,3′,4′-tetramethoxy-3-phenylcoumarin (XIII) becomes still more evident from the fact that the ketone (X) obtained from the oxidation of tetramethyl-acacatechin (IX) is in every re-

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[12] Kostanecki, Lampe and Tambor, *Ber.*, 37, 1402 (1904).

spect identical with the same substance previously synthesized by the action of diazomethane on 2,4,6,3′,4′-pentamethoxy-α,α-diphenyl-acetyl chloride with subsequent closure of the ring.[13] This was proved by the direct comparison of the two substances entailing the repetition of the synthesis of the ketone owing to the lack of the original material prepared in 1921.

Attempts to oxidize the α-diketone with neutral permanganate to a pyruvic acid or a maclurin derivative[14] have been disappointing as the products obtained were 6-hydroxy-2,4,3′,4′-tetramethoxy-α,α-diphenylacetic[15] and formic acids. The production of the latter substance is, however, of some interest as it emphasizes the absence of a phenyl group in the 1-position as required by Formula I for catechin. In this connection it is also interesting to note that Gauthier[16] has already recorded the production of formic acid from catechin and that this was not confirmed by Miller.[17]

The production of 6-hydroxy-2,4,3′,4′-tetramethoxy-α,α-diphenylacetic acid by the action of neutral permanganate on the α-diketone seemed to some extent contradictory to the fact that only dimethylphloroglucinol and veratric acid are produced by the oxidation of tetramethyl-acacatechin with permanganate in alkaline solution.[18] A quantitative study of this reaction has, however, shown that 6-hydroxy-2,4,3′,4′-tetramethoxy-α,α-diphenylacetic acid is produced under these conditions and that the dimethylphloroglucinol and veratric acid are only secondary oxidation products which are formed from the diphenylacetic acid derivative. That this is the case was confirmed by the action of alkali and potassium permanganate on 2,4,6,3′,4′-pentamethoxy-α,α-diphenylacetic acid and pentamethyl-maclurin, respectively, when trimethylphloroglucinol and veratric acid were obtained. In this connection it might be mentioned that the formation of these disintegration products from pentamethyl-maclurin corresponds to the production of phloroglucinol and protocatechuic acid from maclurin.[19]

From these observations it may be concluded that the fission of the chroman nucleus precedes oxidation and this was confirmed as follows. Pentamethyl-acacatechin (XIV) was reacted on with alcoholic potassium hydroxide and methyl iodide or dimethyl sulfate, respectively, when Substance XV was obtained. This latter substance yielded 2,4,6,3′,4′-pentamethoxy-α,α-diphenylacetic acid (XVI) on oxidation. Substance XV was also synthesized according to Formulas XVII, XVIII and XIX.

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[13] Nierenstein, *J. Chem. Soc.*, **119**, 167 (1921).

[14] Compare Hazleton and Nierenstein, This Journal, **46**, 2100 (1924).

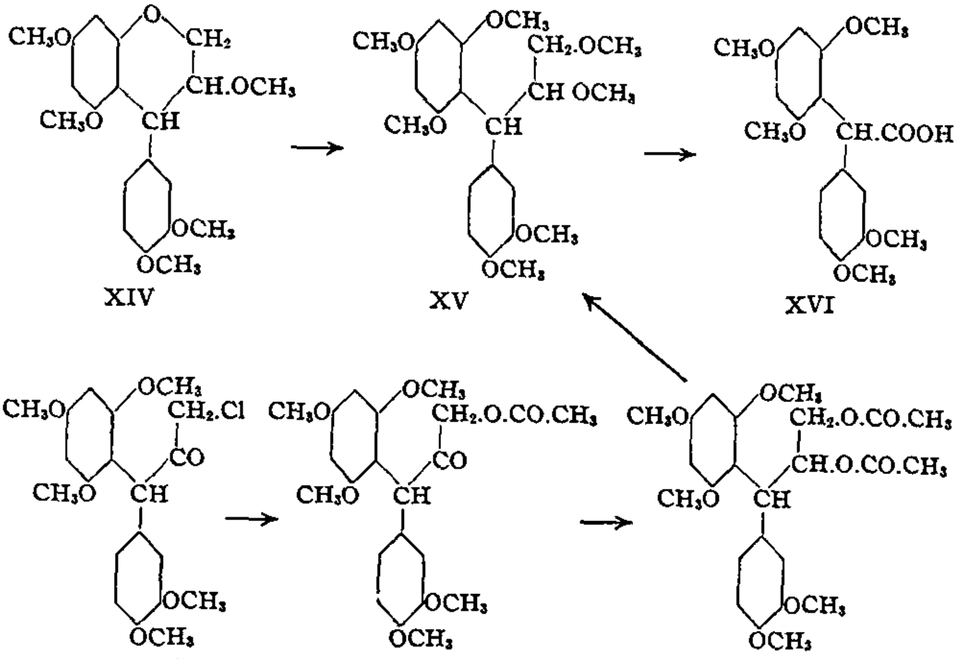
[15] Nierenstein, *J. Chem. Soc.*, **117**, 1154 (1920).

[16] Gauthier, *Bull. soc. chim.*, [ii] **30**, 567 (1878).

[17] Miller, *Ann.*, **220**, 115 (1883).

[18] (a) Perkin, *J. Chem. Soc.*, **87**, 400 (1905). (b) Nierenstein, *ibid.*, **121**, 610 (1922).

[19] Hlasiwetz and Pfaundler, *Ann.*, **127**, 352 (1863).



The work on catechin published from this Laboratory has been constantly criticized by Freudenberg and his collaborators. Some of the older criticisms have been dealt with in previous communications[20] but reference must be made to a recent publication by Freudenberg and Purrmann.[21] These authors have come to the conclusion that acacatechin (m. p., 204–205°) is a mixture consisting of *dl*-catechin, *l*-catechin and *l*-epicatechin. These contentions are based (1) on the statement that Freudenberg[22] has examined an original specimen of acacatechin sent him by A. G. Perkin, the receipt of which had been acknowledged by Freudenberg, Böhme and Beckendorf[23] and (2) that the melting point 152–153°, found by Perkin[24] for natural and by Nierenstein[25] for synthetic tetramethyl-acacatechin is not correct, since *dl*-tetramethyl-acacatechin melts at 142° and not at 152–153°, the latter melting point being that of tetramethyl-*l*-epicatechin. It must therefore be noted: (1) that the material received by Freudenberg, Böhme and Beckendorf, who state: "wir danken Hrn. A. G. Perkin für die Übersendung einer Probe seines Kath" was not acacatechin but the cutch used by Perkin in his work on acacatechin; (2) that the ether ex-

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[20] Ref. 15, p. 1156. Ref. 18b, p. 607. Nierenstein, *Ber.*, 55, 3831 (1922). Ref. 14, p. 2101.

[21] Freudenberg and Purrmann, *Ann.*, 437, 278 (1924).

[22] Freudenberg, *Ber.*, 55, 1938 (1922).

[23] Freudenberg, Böhme and Beckendorf, *Ber.*, 54, 1205 (1921).

[24] Ref. 18a, p. 404.

[25] Nierenstein, *J. Chem. Soc.*, 119, 166 (1921).

traction used by Freudenberg in the preparation of acacatechin from cutch gives different results from the ethyl acetate extraction employed by Perkin. This has frequently been observed in this Laboratory with the result that ethyl acetate only is used in the preparation of catechin by us. In agreement with Freudenberg we find that ether extractions of Indian cutches yield mixtures of varying melting points. These catechin preparations, however, can be purified by crystallization from dil. acetic acid. The acacatechin thus obtained melts at 204–205° and gives the following derivatives: penta-acetyl derivative, m. p., 160°; tetramethyl derivative, m. p., 152–153°; and acetyl-tetramethyl derivative, m. p., 136–137°; these are in agreement with the data recorded by Perkin for natural and by Nierenstein for synthetic acacatechin.[26] It must further be noted (3) that the low melting point 142° recorded by Freudenberg and Purrmann for tetramethyl-acacatechin is due to the presence of traces of the heptamethyl derivative XV which is formed when acacatechin is methylated with dimethyl sulfate and alkali. The production of low-melting tetramethyl-acacatechin has also been observed by us, but it has always been found that such low-melting preparations contained varying amounts of the heptamethyl derivative. These preparations melted, however, at 152–153° when freed from the heptamethyl derivative. Finally, (4) it has already been mentioned that during the course of the present investigation it had been found necessary to repeat the synthesis of the ketone X. In view of the criticism of Freudenberg and Purrmann it was thought desirable to reduce the ketone X to tetramethyl-acacatechin as previously described.[27] The tetramethyl-acacatechin, *the synthesis of which has thus been repeated* melted at 152–153° and this melting point was not depressed on admixture with optically-inactive tetramethyl-acacatechin (m. p., 152–153°). The same result was obtained on admixture of the synthetic acetyl-tetramethyl-acacatechin (m. p., 136–137°, as previously recorded) with the natural product. In view of these observations the recommendation of Freudenberg and Purrmann that the synthetic acacatechin should be crossed out from the literature can scarcely be upheld.

Reference must also be made to a recent publication by Ryan and his collaborators[28] who have favored Formula I for catechin since 1916.[29] These authors have repeated the reduction and subsequent methylation

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[26] In the exhaustive fractionation of extracts from catechin-producing acacias, an account of which will shortly be published, a large number of fractions have been obtained which melt at 204–205°. It would hardly be expected that this melting point would be so consistently reproduced, and that by successive fractions, if it were that of a fortuitous mixture as suggested by Freudenberg.

[27] Ref. 13, p. 168.

[28] Drumm, O'Reilly and Ryan, *Proc. Roy. Irish Acad.*, 37, 19 (1925).

[29] Ryan and Walsh, *Sci. Proc. Roy. Dublin Soc.*, 15, 113 (1916). Drumm, McMahon and Ryan, *Proc. Roy. Irish Acad.*, 36, 149 (1924).

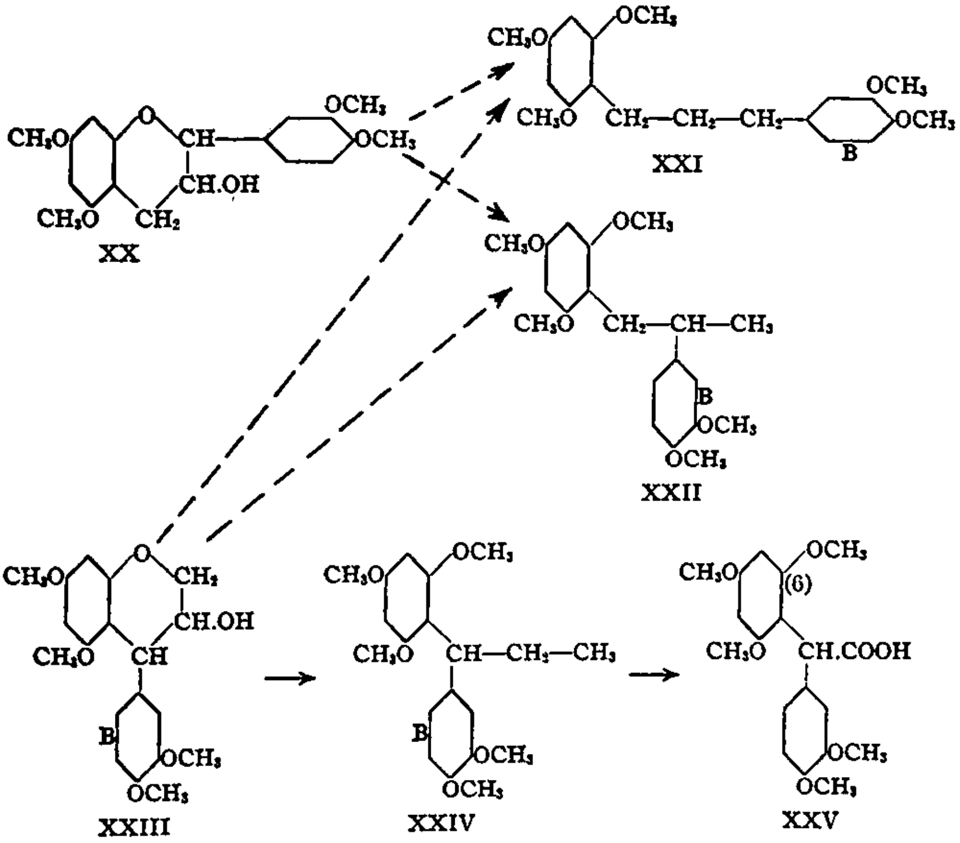
of tetramethyl-gambiercatechin described by Kostanecki and Lampe,[30] and have obtained a product which melted at 87–88°. They have also synthesized 2,4,6,3′,4′-pentamethoxy-α,γ-diphenylpropane (XXI) and 2,4,6,3′,4′-pentamethoxy-α,α-diphenylpropane (XXIV). The following is a summary of the melting points obtained by Drumm, O'Reilly and Ryan as compared with those found by previous workers.

Table I

Melting Points, °C.

	Methylated reduction product	α,α-Deriv.	α,γ-Deriv.
Kostanecki	83–84	...	...
Ryan and Walsh	83–84	...	...
Nierenstein	83–84	83–84	87–88
Freudenberg	87–88	...	87–88
Drumm, O'Reilly and Ryan	87–88	80–81	87–88

As will be realized from this summary the data obtained by Drumm, O'Reilly and Ryan go to show that the methylated reduction product of Kostanecki is identical with 2,4,6,3′,4′-pentamethoxy-α,γ-diphenylpropane



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[30] Kostanecki and Lampe, *Ber.*, 40, 720 (1907).

(XXI) as required by Formula I for catechin[31] and this is still further confirmed by the fact that the melting point of the α,γ-derivative is not depressed on admixture with Kostanecki's methylated reduction product.

These results are bewildering and the whole issue becomes still more confused now that Freudenberg and his collaborators[3] have shown that not only 2,4,6,3′,4′-pentamethoxy-α,γ-diphenylpropane (XXI) but also 2,4,6-3′,4′-pentamethoxy-α,β-diphenylpropane (XXII) may be produced from tetramethyl-catechin (XX, according to Freudenberg).

These observations seem to indicate that the nucleus B in tetramethyl-acacatechin (XXIII) is mobile which leads under various conditions to the production of XXIV, XXII and XXI, respectively, which would thus, perhaps, account for the different results obtained by the various workers. In any case it is evident that very little can be learned as to the constitution of catechin from Kostanecki's methylated reduction product. Far greater importance must be attached to the formation of 2,4,6,3′,4′-pentamethoxy-α,α-diphenylacetic acid (XXV) and 6-hydroxy-2,4,3′,4′-tetramethoxy-α,α-diphenylacetic acid, respectively, as these products have now been obtained under the following different conditions.

6-Hydroxy-2,4,3′,4′-tetramethoxy-α,α-diphenylacetic acid.—(1) By the reduction of tetramethyl-acacatechin and oxidation.[15] (2) By the oxidation of the α-diketone (XII) described in the present communication. (3) By the oxidation of tetramethyl-acacatechin with permanganate in alkaline solution, also described in the present communication.

2,4,6,3′,4′-Pentamethoxy-α,α-diphenylacetic acid.—(1) By the reduction of tetramethyl-acacatechin, methylation and oxidation.[32] (2) By the fission of the chroman nucleus, preparation of the heptamethyl derivative (XV) and oxidation, described in the present communication.

From these results one is forced to assume that 2,4,6,3′,4′-pentamethoxy-α,α-diphenylpropane is the *normal* disintegration product, especially if one also considers that acacatechin is known to yield maclurin.[33]

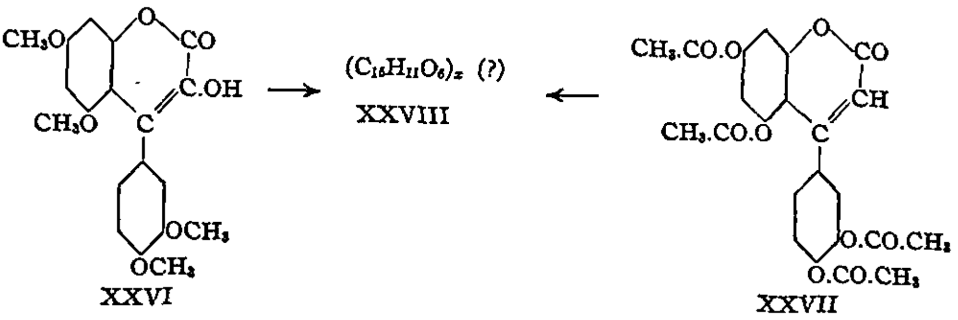
In this connection reference must also be made to the fact that 2-hydroxy-4,6,3′,4′-tetramethoxy-3-phenylcoumarin (XXVI) yields on demethylation with hydriodic acid the same product that has been obtained by Ciamician and Silber[34] by the action of hydriodic acid on 4,6,3′,4′-tetra-acetoxy-3-phenylcoumarin (XXVII). Although it has so far not been possible to elucidate the constitution of Substance XXVIII an interesting link has been established between Substances XXVI and XXVII, the latter of which is obtained by the action of acetic anhydride on maclurin. This again emphasizes the α,α-diphenylpropane structure of acacatechin.

[31] Compare Freudenberg, *Ber.*, **53**, 1416 (1920).

[32] Nierenstein, *J. Chem. Soc.*, **117**, 977 (1920).

[33] Ref. 14, p. 2101.

[34] Ciamician and Silber, *Ber.*, **27**, 1630 (1894).



XXVI $\longrightarrow$ XXVIII $\longleftarrow$ XXVII

Experimental Part

The acetone used in these experiments was refluxed for some time with alkali and potassium permanganate and then distilled. The "neutral permanganate" solution consisted of 850 cc. of *N* potassium permanganate solution and 15 g. of magnesium sulfate dissolved in 150 cc. of water.

4,6,3',4'-Tetramethoxy-3-phenylchroman-2-one (X).—*To a boiling solution of* 10 g. of tetramethyl-acacatechin in 100 cc. of acetone is added 130 cc. of "neutral permanganate" and the solution is heated for two hours. The filtered solution, to which are added the acetone washings of the manganese oxide, deposits on standing a small quantity of Substance X, but the main bulk (68%, average of four experiments) is obtained on concentration to about 50 cc. As already stated the product thus obtained is in every respect identical with synthetic 4,6,3',4'-tetramethoxy-3-phenylchroman-2-one (X), previously described.[13]

Anal. Subs., 7.24 mg.: CO_2, 17.60; H_2O, 3.93. Calcd. for $C_{19}H_{20}O_6$: C, 66.27; H, 5.81. Found: C, 66.29; H, 6.07.

The phenylhydrazone already described[13] and the *p*-bromophenylhydrazone were also prepared from both substances and they were also found to be identical. The *p-bromophenylhydrazone* crystallizes from glacial acetic acid in brown, thick needles, which melt at 257–259°, with decomposition.

Anal. Subs., 8.10 mg.: N, 0.361 cc. (21°, 752 mm.). Calcd. for $C_{25}H_{25}O_5N_2Br$: N, 5.45. Found: 5.12.

The filtrate from the crude product (X) leaves on evaporation an oily residue which on standing solidifies to a yellow solid. The latter is a mixture and consists of unchanged tetramethyl-acacatechin, 4,6,3',4'-tetramethoxy-3-phenylchroman-2-one (X), 4,6,3',4'-tetramethoxy-3-phenylchroman-1,2-dione (XII), 2-hydroxy-4,6,3',4'-tetramethoxy-3-phenylcoumarin (XIII), 6-hydroxy-2,4,3',4'-tetramethoxy-α,α-diphenylacetic acid and some resinous by-product.

The separation of these substances may be carried out as follows. The solid is dissolved in ether and the ethereal solution shaken with aqueous sodium bicarbonate, saturated with carbon dioxide. The aqueous solution thus obtained yields 6-hydroxy-2,4,3',4'-tetramethoxy-α,α-diphenylacetic acid (7.2%, average of three experiments) on acidification, extraction with ether and evaporation of the solvent. The ethereal solution left after separation of the aqueous solution containing the sodium salt of the α,α-diphenylacetic acid derivative is evaporated to dryness at room temperature and the remaining solid dried over phosphorus pentoxide. The product is then powdered, mixed with an excess of sand, and extracted in a small Soxhlet in turn with (1) chloroform, which extracts mainly 4,6,3',4'-tetramethoxy-3-phenylchroman-1,2-dione (4.1%, average of two experiments), (2) benzene, which removes to a large extent 2-hydroxy-4,6,3',4'-tetramethoxy-3-phenylcoumarin (2.8%, average of two experiments), (3) ether and (4) alcohol, which extract mixtures, consisting of unchanged tetramethylacacatechin (2.7%, average of three experiments), 4,6,3′,4′-tetramethoxy-3-phenylchroman-2-one (2.1%, average of three experiments) and the resinous by-product (4%, average of two experiments).

Isonitroso-4,6,3′,4′-tetramethoxy-3-phenylchroman-2-one (XI).—A solution of 2 g. of the ketone (X) in 50 cc. alcohol, mixed with 3 g. of amyl nitrite and 12 cc. of concd. hydrochloric acid is heated for one hour and then poured into water. The solid thus obtained is dissolved in alkali, the solution filtered and acidified with acetic acid, when a faintly yellow solid is obtained. The latter crystallizes from benzene in sheath-like plates which melt at 116°. The product is soluble in the usual organic solvents and also slightly in water. Alkali produces a yellow solution, which becomes colorless on acidification. Yield, 88%, average of five experiments.

Anal. Subs., 7.47 mg.: N, 0.241 cc. (21°, 763 mm.). Calcd. for $C_{19}H_{19}O_7N$: N, 3.75. Found: 3.76.

2-Hydroxy-4,6,3′,4′-tetramethoxy-3-phenylcoumarin (XIII).—Three g. of the isonitroso derivative, dissolved in 30 cc. of glacial acetic acid is heated for 45 minutes over a free flame with 30 cc. of 10% sulfuric acid. On standing the flask becomes filled with a yellow solid from which the deep yellow solution is filtered by suction. On crystallization from alcohol, colorless, glittering needles are obtained which melt at 181°. The product is sparingly soluble in methyl and ethyl alcohols and ethyl acetate, but more soluble in glacial acetic acid and quite insoluble in the other organic solvents. It dissolves in cold alkali forming a deep yellow solution which turns saffron-yellow on warming. In concd. sulfuric acid an orange solution is produced which turns yellow on dilution. The alcoholic solution turns deep red on the addition of ferric chloride. Yield, 91%, average of four experiments.

Anal. Subs., 9.61 mg.: CO_2, 22.41; H_2O, 4.31. Calcd. for $C_{19}H_{18}O_7$: C, 63.69; H, 5.02. Found: C, 63.60; H, 5.03.

The ACETYL DERIVATIVE crystallizes from alcohol in small needles; m. p., 153°.

Anal. Subs., 17.42 mg.: CO_2, 40.19; H_2O, 8.08. Calcd. for $C_{21}H_{20}O_8$: C, 63.00; H, 5.00. Found: C, 62.92; H, 5.19.

2,4,6,3′,4′-Pentamethoxy-3-phenylcoumarin is prepared by the action of diazomethane or methyl iodide and silver oxide on the ethereal solution of Substance XIII, but no methylation takes place by the interaction with alkali and dimethyl sulfate in alcoholic solution. The product crystallizes from alcohol in small needles which melt at 146°.

Anal. Subs., 11.53 mg.: CO_2, 27.26; H_2O, 5.62. Calcd. for $C_{20}H_{20}O_7$: C, 64.52; H, 5.38. Found: C, 64.47; H, 5.46.

TABLE II

COMPARISON BETWEEN 2-HYDROXY-4,6,3′,4′-TETRAMETHOXY-3-PHENYLCOUMARIN AND 4,6,3′,4′-TETRAMETHYL-QUERCETIN

	M. p., °C.	Ref.
2-Hydroxy-4,6,3′,4′-tetramethoxy-3-phenylcoumarin	181	..
4,6,3′,4′-Tetramethyl-quercetin	197–198	12
2-Acetoxy-4,6,3′,4′-tetramethoxy-3-phenylcoumarin	153	..
Acetyl-4,6,3′,4′-tetramethyl-quercetin	160–163	35
2,4,6,3′,4′-Pentamethoxy-3-phenylcoumarin	146	..
Pentamethyl-quercetin	148	36
	150–151	37

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[35] Herzig, *Monatsh.*, 33, 683 (1912).

[36] Waliaschko, *Arch. Pharm.*, **242**, 225 (1904).

[37] Perkin, *J. Chem. Soc.*, **103**, 1632 (1913).

Mixed melting points of 2,4,6,3′,4′-pentamethoxy-3-phenylcoumarin with authentic pentamethyl-quercetin (m. p., 150°) give depressions of 17° to 21°.

Action of Alkali on 2-Hydroxy-4,6,3′,4′-tetramethoxy-3-phenylcoumarin. (XIII).—Three g. of the substance is heated for ten minutes in a silver dish with 8 g. of powdered sodium hydroxide and a little water. The solid is dissolved in water, and the solution acidified with dil. sulfuric acid, filtered and extracted with ether. The ethereal extract is then shaken with aqueous sodium bicarbonate, saturated with carbon dioxide and the two layers are examined separately.

The *ethereal* layer is dried for some time over anhydrous sodium sulfate and then treated with an excess of diazomethane. The oil left on evaporation of the ether solidifies immediately on inoculation with trimethyl-phloroglucinol; the substance forms long needles from ligroin (b. p., 50–60°) which melt at 52°. This melting point is not depressed on admixture of the substance with authentic trimethyl-phloroglucinol.

The *aqueous* layer is acidified and extracted with ether, which leaves veratric acid (m. p. and mixed m. p., 180°) on evaporation.

Attempt to Demethylate 2-Hydroxy-4,6,3′,4′-tetramethoxy-3-phenylcoumarin. (XIII).—One g. of the substance is heated with 15 cc. of hydriodic acid (d., 1.7) and 3 cc. of acetic anhydride. The product crystallizes from water in faintly yellow needles; m. p., 162–163°. It dissolves in alkali forming a yellow solution and gives a green-yellow coloration with concd. sulfuric acid.

Anal. Subs., 5.40; 8.64 mg.: CO_2, 12.32, 19.70; H_2O, 1.75, lost. Found: C, 62.22, 62.18; H, 3.63.

The analytical data do not agree with those required for 2,4,6,3′,4′-pentahydroxy-3-phenylcoumarin, namely, C, 59.57; H, 3.34. They are, however, in agreement with formula $(C_{15}H_{11}O_6)_x$, which requires further study. They are also in fair agreement with some of the data given by Ciamician and Silber[34] for their product obtained by the action of hydriodic acid on 4,6,3′,4′-tetra-acetoxy-3-phenylcoumarin: C, 62.15, 62.20, 61.86, 61.14; H, 3.67, 3.53, 3.69, 3.87. The melting point given by Ciamician and Silber is, however, 270° and not 162–163°. The substance was, therefore, also prepared according to the method of Ciamician and Silber, when it was found to melt at 162–163°. The identity was also established by the mixed melting point of the two substances which showed no depression. The melting point 270° is apparently a clerical error which should, perhaps, have read 170°. The product was not further investigated.

4,6,3′,4′-Tetramethoxy-3-phenylchroman-1,2-dione (XII).—This product is obtained in small quantities during the oxidation of tetramethyl-acacatechin and the hydrolysis of the isonitroso derivative, but it is best prepared by the oxidation of 4,6,3′,4′-tetramethoxy-3-phenylchroman-2-one.

1. To a solution of 10 g. of 4,6,3′,4′-tetramethoxy-3-phenylchroman-2-one in 100 cc. of acetone is added 130 cc. of "neutral permanganate" and the solution heated for two hours. The solution is filtered, the manganese oxide washed with warm acetone and the solution concentrated to about 25 cc. A small quantity of unchanged 4,6,3′,4′-tetramethoxy-3-phenylchroman-2-one separates on standing in ice. The filtered solution is evaporated to dryness, dissolved in ether and freed from 6-hydroxy-2,4,3′,4′-tetramethoxy-α,α-diphenylacetic acid (22.7%, average of three experiments) as previously described. The solid left on evaporation of the ether consists mainly of 4,6,3′,4′-tetramethoxy-3-phenylchroman-1,2-dione (XII), but it contains also 2-hydroxy-4,6,3′,4′-tetramethoxy-3-phenylcoumarin (XIII) and some resinous by-product. The solid is dissolved in carbon tetrachloride from which the 4,6,3′,4′-tetramethoxy-3-

phenylchroman-1,2-dione crystallizes in long, bright yellow needles, which melt at 134° (16.3%, average of three experiments). A further quantity (5.7%, average of three experiments) of Substance XII is obtained on concentration of the carbon tetrachloride solution. The substance obtained on evaporation to dryness consists of a resinous semisolid, which yields on prolonged treatment with ligroin practically colorless 2-hydroxy-4,6,3',4'-tetramethoxy-3-phenylcoumarin (47%, average of two experiments).

Anal. Subs., 10.62 mg.: CO_2, 24.78; H_2O, 4.88. Calcd. for $C_{19}H_{18}O_7$: C, 63.69; H, 5.02. Found: C, 63.64; H, 5.14.

An attempt to condense the α-diketone (XII) with toluene-3,4-diamine gave no definite condensation product, but the interaction with diazomethane in ethereal solution leads to the production of *1,2-methylenedioxy-4,6,3',4'-tetramethoxy-3-phenylchroman.*[18] This forms faintly yellow needles from dil. alcohol; m. p., 122°; yield, 95%.

Anal. Subs., 10.08 mg.: CO_2, 25.53; H_2O, 5.26. Calcd. for $C_{20}H_{20}O_7$: C, 64.52; H, 5.38. Found: C, 64.47; H, 5.45.

2. The isolation of 4,6,3',4'-tetramethoxy-3-phenylchroman-1,2-dione (XII) during the oxidation of tetramethyl-acacatechin has already been described under the preparation of Substance X. As regards the isolation of Substance XII formed during hydrolysis of the isonitroso derivative (XI) the following method was found to give the best results. The yellow filtrate obtained from the crude 2-hydroxy-4,6,3',4'-tetramethoxy-3-phenylcoumarin (XIII) is shaken for some time with carbon tetrachloride and the carefully dried carbon tetrachloride solution diluted with ligroin until a permanent cloudiness is obtained. On standing, a small quantity (about 1.5%, average of two experiments) of the α-diketone crystallizes; m. p., 130–131°. This melting point is raised to 134° on crystallization from carbon tetrachloride.

Interconversion of 4,6,3',4'-Tetramethoxy-3-phenylchroman-1,2-dione (XII) and 2-Hydroxy-4,6,3',4'-tetramethoxy-3-phenylcoumarin (XIII).—The interconversion of these desmotropic substances may be observed as follows.

1. The α-diketone crystallizes from carbon tetrachloride in yellow needles; m. p., 134°. When, however, alcohol is added to the carbon tetrachloride solution, not the yellow α-diketone but the colorless enol, melting at 181°, is obtained.

2. The colorless enol may also be crystallized from carbon tetrachloride from which it separates in colorless needles which melt at 181°, but when dry acetone is added to the solution the yellow α-diketone, melting at 134°, is obtained.

3. The yellow α-diketone when dissolved in alcohol gives the colorless enol, melting at 181°.

4. The colorless enol separates from acetone as the yellow α-diketone, melting at 134°.

5. Reference has already been made to the deep red coloration which is obtained by the addition of ferric chloride to the alcoholic solution of the enolic product. This coloration may be used in the following manner to demonstrate the conversion of the α-diketone into the enol. To a solution of the α-diketone in acetone a few drops of ferric chloride are added, when the solution turns faintly red, and this coloration becomes deeper on standing. When, however, a few drops of alcohol are added to the acetone solution the production of the deep red color is instantaneous.

From these results one may conclude that (1) both the ketonic and enolic forms are stable in carbon tetrachloride, (2) alcohol favors the enolic form and (3) acetone favors the ketonic form.

Oxidation of 4,6,3',4'-Tetramethoxy-3-phenylchroman-1,2-dione (XII).—A solu-

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[18] Compare Nierenstein, *J. Chem. Soc.*, **107**, 870 (1915). Dean and Nierenstein, *ibid.*, **117**, 803 (1920). Biltz and Paetzold, *Ann.*, **433**, 71 (1923).

tion of 6 g. of the α-diketone in 100 cc. of acetone is oxidized with 100 cc. of "neutral permanganate" for two hours, the mixture filtered and the manganese oxide washed with hot acetone. No solid is formed even on concentration to a small bulk and the solution is concentrated to dryness at room temperature. The solid obtained is triturated with dil. sulfuric acid and dissolved in ether. The ethereal extract is shaken with aqueous sodium bicarbonate saturated with carbon dioxide and the aqueous extract examined separately. In this connection it is interesting to note that the ethereal layer leaves nothing on evaporation, which thus indicates that nothing but acidic disintegration products are obtained.

The aqueous layer is acidified and steam-distilled. The distillate contains formic acid; it reduces silver nitrate and mercuric chloride and precipitates cerium nitrate.[39]

In a second experiment using 6 g. of the α-diketone the formic acid was kindly estimated by Dr. R. C. Menzies,[40] who found 0.5425 g. of formic acid by titration with 0.1 *N* thallium hydroxide using phenolphthalein as indicator. This corresponds to 104.85% as required by calculation. On evaporation of the liquid to dryness in a vacuum over concd. sulfuric acid a crystalline solid was obtained. The analysis of the crude substance gave Tl = 80.97%. The product crystallized from alcohol gave Tl = 82.04%, whereas thallium formate requires 81.95%. An authentic specimen of thallium formate gave Tl = 81.70%. From these experiments one may conclude that traces of some other acid, probably acetic acid which is produced from the acetone[41] are also present, but that formic acid is mainly produced.

The solution left after the formic acid is removed on steam distillation contains 6-hydroxy-2,4,3′,4′-tetramethoxy-α,α-diphenylacetic acid (93%, average of two experiments). For further identification the 6-ethoxy-2,4,3′,4′-tetramethoxy-α,α-diphenylacetic acid, which had previously been obtained only in a very small quantity,[42] was also prepared. It melted at 138°, which is in good agreement with the melting point 137–138° previously recorded.

Oxidation of Tetramethyl-acacatechin (IX) in Alkaline Solution with Potassium Permanganate.—*Four experiments were made, using 10 g. of tetramethyl-acacatechin.* In two of these experiments the tetramethyl-acacatechin was suspended in alkali and the potassium permanganate added, so that there was always an excess of alkali. In the other two the product was suspended in potassium permanganate and the alkali added, the potassium permanganate thus being in excess. A solution of 40 g. of sodium hydroxide in 250 cc. of water and 1850 cc. of normal potassium permanganate solution was used for each oxidation which was carried out in a boiling water bath for 9½ hours. The following disintegration products were identified.

Table III

	Excess of alkali		Excess of $KMnO_4$	
	I, g.	*II*, g.	*III*, g.	*IV*, g.
Dimethyl-phloroglucinol	1.5	0.7	1.8	2.3
6-Hydroxy-2,4,3′,4′-tetramethoxy-α,α-diphenylacetic acid	2.7	3.1	1.9	0.6
Veratric acid	1.8	2.1	2.7	1.7
4,6,3′,4′-Tetramethoxy-3-phenylchroman-2-one	...	0.2	2.8	1.9

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[39] Compare Rosenthaler, "Der Nachweis organischer Verbindungen," F. Enke, Stuttgart, 1914, p. 27.

[40] Compare Christie and Menzies, *J. Chem. Soc.*, 127, 2369 (1925).

[41] Compare Evans and Nicoll, This Journal, 47, 2789 (1925).

[42] Ref. 14, p. 2104.

The following is the procedure for the identification of the above mentioned substances.

1. The alkaline solution is filtered hot and the manganese oxide is washed several times with hot water, about 800 cc. of water being used. The manganese oxide is carefully dried and exhaustively extracted with ether. The ethereal extract thus obtained contains some unchanged tetramethyl-acacatechin (1.3 g., average of three experiments) and 4,6,3',4'-tetramethoxy-3-phenylchroman-2-one, which are separated from each other by several crystallizations from acetone when the 4,6,3',4'-tetramethoxy-3-phenylchroman-2-one is first obtained.

2. The alkaline filtrate is exhaustively extracted with ether and the ethereal extract dried over anhydrous sodium sulfate. On evaporation of the ether a small quantity of 4,6,3',4'-tetramethoxy-3-phenylchroman-2-one and traces of tetramethyl-acacatechin are obtained.

3. The aqueous alkaline solution is acidified and exhaustively extracted with ether. The ethereal extract is shaken with aqueous sodium bicarbonate saturated with carbon dioxide and separated from the ethereal layer. The latter is dried over anhydrous sodium sulfate and treated with an excess of diazomethane. Trimethyl-phloroglucinol is obtained on evaporation of the ether, from which the amount of dimethyl-phloroglucinol obtained is calculated.

4. The aqueous layer left after the removal of the dimethyl-phloroglucinol is acidified and extracted with ether, dried over anhydrous sodium sulfate and evaporated to dryness. The solid left is dissolved in absolute alcohol[43] and saturated with dry hydrogen chloride, heated for a short time and again treated with hydrogen chloride. This is repeated thrice and the alcohol then removed in a vacuum. The residue is again dissolved in absolute alcohol and once more treated with dry hydrogen chloride. The solid left on evaporation of the alcohol under diminished pressure is redissolved in absolute alcohol, the alcohol distilled in a vacuum and the residue dissolved in about 400 cc. of ether. The ethereal solution is then shaken with 100 cc. of 5% sodium hydroxide solution, any rise of temperature being carefully avoided. The alkaline solution thus obtained yields 6-hydroxy-4,6,3',4'-tetramethoxy-α,α-diphenylacetic acid when warmed, extracted with ether and the ethereal solution evaporated.

5. The ethereal extract obtained on the separation of the 6-hydroxy-4,6,3',4'-tetramethoxy-α,α-diphenylacetic acid leaves a semisolid residue on evaporation of the ether. This solid gives veratric acid when warmed with dil. alkali, subsequent acidification with dil. hydrochloric acid, extraction with ether and evaporation of the ether.

Oxidation of 2,4,6,3',4'-Pentamethoxy-α,α-diphenylacetic acid (XVI) in Alkaline Solution with Potassium Permanganate.—A solution of 25 g. of 2,4,6,3',4'-pentamethoxy-α,α-diphenylacetic acid in 250 cc. of water is oxidized in a boiling water-bath with 25 g. of sodium hydroxide and 850 cc. of normal potassium permanganate solution. The alkaline filtrate to which are added the washings of the manganese oxide yields trimethyl-phloroglucinol on steam distillation; yield of crude material, 10.84 g., or 93.2%. The solution left after the removal of the trimethyl-phloroglucinol is acidified and extracted with ether. The solid obtained on evaporation consists mainly of veratric acid, but it contains traces of 2,4,6,3',4'-pentamethoxy-α,α-diphenylacetic acid. Sharply melting veratric acid (9.7 g., or 76.8%) and 2,4,6,3',4'-pentamethoxy-α,α-diphenylacetic acid (1.3 g.) are obtained on several fractional crystallizations from dil. alcohol.

Action of Potassium Permanganate and Alkali on Pentamethyl-maclurin.—Ten g. of pentamethyl-maclurin is oxidized with 10 g. of sodium hydroxide and 650 cc. of *N*

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[43] The alcohol was refluxed over calcium oxide, dried over calcium carbide and distilled.

potassium permanganate solution in the manner described in the case of the α,α-acetic acid; yields, 3.7 g. of crude trimethyl-phloroglucinol (72.6%), 4.1 g. of crude veratric acid (74.5%) and 1.2 g. of pentamethyl-maclurin. In this connection it is interesting to note that benzophenone may be converted under the same conditions to benzoic acid. An experiment using 5 g. of benzophenone gave 1.7 g. of benzoic acid.

Pentamethyl-acacatechin (XIV).—Twenty-five g. of acetyl-tetramethyl-acacatechin (m. p., 136–137°) dissolved in methyl alcohol is methylated with 29 g. of dimethyl sulfate and 13 g. of potassium hydroxide. The solid obtained on pouring the mixture into water is dried over phosphorus pentoxide and exhaustively extracted in a Soxhlet apparatus with ligroin (b. p., 80–90°). On concentration of the ligroin solution, fine, silky needles are obtained which melt at 107° and this melting point is not raised on successive crystallizations of the substance from ligroin, chloroform, carbon tetrachloride and dil. alcohol. The solid left after removal of the pentamethyl-acacatechin consists of β,γ,2,4,6,3′,4′-heptamethoxy-α,α-diphenylpropane (XV) and tetramethyl-acacatechin. The average yields in two experiments were: 16.5 g. of pentamethyl-acacatechin, 2.1 g. of tetramethyl-acacatechin and 1.8 g. of β,γ,2,4,6,3′,4′-heptamethoxy-α,α-diphenylpropane.

Anal. Subs., 10.42 mg.: CO_2, 25.36; H_2O, 6.37. Calcd. for $C_{20}H_{24}O_6$: C, 66.66; H, 6.66. Found: C, 66.37; H, 6.84.

β,γ,2,4,6,3′,4′-Heptamethoxy-α,α-diphenylpropane (XV).—This substance can be obtained by the following methods.

1. A solution of 20 g. of pentamethyl-acacatechin in 100 cc. of alcohol is heated on a boiling water-bath for 8–10 hours with 25 cc. of 25% alcoholic potassium hydroxide and 11 g. of methyl iodide. The solution is then poured into water and freed from alcohol by standing in a boiling water-bath. The solid thus obtained is crystallized from alcohol from which it separates in small cubes which melt at 122°. The average yield of two experiments is 87%.

2. Ten g. of pentamethyl-acacatechin, dissolved in 50 cc. of alcohol is heated under the above-mentioned conditions with 25 cc. of 25% alcoholic potassium hydroxide and 12 g. of dimethyl sulfate. The average yield of three experiments is 91%.

3. The product is formed during the preparation of tetramethyl-acacatechin by the action of dimethyl sulfate on acacatechin. Low-melting tetramethyl-acacatechin is freed from it in the following manner. The product dried over phosphorus pentoxide is dissolved in four times its weight of dry carbon tetrachloride; to this solution ligroin is added until a faint cloudiness appears when, on standing, various amounts of the heptamethoxy derivative crystallize. After filtration a fresh amount of ligroin is added when again a small quantity of the heptamethoxy derivative crystallizes. The tetramethyl-acacatechin obtained on evaporation of the carbon tetrachloride crystallizes from alcohol and melts at 152–153°.

4. Reference has already been made to the production of β,γ,2,4,6,3′,4′-heptamethoxy-α,α-diphenylpropane and tetramethyl-acacatechin during the production of pentamethyl-acacatechin from acetyl-tetramethyl-acacatechin. The separation of the two substances is carried out by dissolving in carbon tetrachloride and precipitating with ligroin as already described.

β,γ,2,4,6,3′,4′-Heptamethoxy-α,α-diphenylpropane is soluble in the usual organic reagents. The addition of ferric chloride to a suspension of the substance in concd. sulfuric acid does not produce either a reddish or a reddish-violet coloration, which seems to be typical for the 3-phenylchroman nucleus only.[44]

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[44] Compare Kostanecki and Lampe, *Ber.*, **39**, 4007 (1906). Greenwood and Nierenstein, *J. Chem. Soc.*, **117**, 1597 (1920). Kahil and Nierenstein, THIS JOURNAL, **46**, 2558 (1924).

Anal. Subs., 0.1532: CO_2, 0.3650; H_2O, 0.1034. Calcd. for $C_{22}H_{30}O_7$: C, 65.02; H, 7.41. Found: C, 64.98; H, 7.55.

On oxidation of 3 g. of β,γ,2,4,6,3′,4′-heptamethoxy-α,α-diphenylpropane with 75 cc. of 20% potassium hydroxide solution and an excess of potassium permanganate, 1.6 g. or a 59.7% yield of 2,4,6,3′,4′-pentamethoxy-α,α-diphenylacetic acid (XVI) is produced.

γ-Acetoxy-2,4,6,3′,4′-pentamethoxy-α,α-diphenylpropane-β-one (XVIII).—A solution of 4 g. of 2,4,6,3′,4′-pentamethoxydiphenyl methyl chloromethyl ketone (XVII)[45] dissolved in 75 cc. of alcohol is heated for six hours with 4.5 g. of potassium acetate. The solid obtained on pouring the mixture into water crystallizes from alcohol in silky needles; m. p., 162°. The product is soluble in the usual organic solvents, but not in benzene or chloroform; yield, 95.9%.

Anal. Subs., 0.1343: CO_2, 0.3113; H_2O, 0.0749. Calcd. for $C_{22}H_{26}O_8$: C, 63.27; H, 6.22. Found: C, 63.35; H, 6.25.

β,γ-Diacetoxy-2,4,6,3′,4′-pentamethoxy-α,α-diphenylpropane (XIX).—Four g. of Substance XVIII dissolved in 75 cc. of acetic anhydride is heated with 15 g. of carefully dried zinc dust for seven hours in an oil-bath at 120–130°. The solution is then filtered and the zinc dust washed with hot acetic acid. The acetic anhydride solution and the acetic acid extract are poured into water and the solid is crystallized from a 2 : 1 mixture of alcohol and acetone. Fine needles are obtained which melt at 173°. The product is soluble in the usual organic solvents; yield, 75%.

Anal. Subs., 0.1547: CO_2, 0.3528; H_2O, 0.0905. Calcd. for $C_{24}H_{30}O_9$: C, 62.17; H, 6.47. Found: C, 62.19; H, 6.54.

Conversion of β,γ-Diacetoxy-2,4,6,3′,4′-pentamethoxy-α,α-diphenylpropane (XIX) into β,γ,2,4,6,3′,4′-Heptamethoxy-α,α-diphenylpropane. (XV).—A boiling solution of 2.5 g. of β,γ-diacetoxy-2,4,6,3′,4′-pentamethoxy-α,α-diphenylpropane in alcohol is treated twice with 15 cc. of 25% potassium hydroxide solution and 10 cc. of dimethyl sulfate. The solid obtained on precipitation with water crystallizes from alcohol in small cubes, which melt at 122° after two crystallizations. This melting point is not depressed on admixture with β,γ,2,4,6,3′,4′-heptamethoxy-α,α-diphenylpropane from pentamethyl-acacatechin.

During these investigations, which covered a period of nearly three years, I was assisted by Miss E. O. Hazleton, and I wish to thank the Department of Scientific and Industrial Research for a grant which has enabled her to take part in this work. My thanks are also due to Dr. G. H. Christie for many valuable suggestions and to the Colston Research Society of the University of Bristol for grants which have covered the expenses of this work.

Summary

1. It is pointed out that the constitution of cyanidin chloride has not been conclusively established and, therefore, its conversion into epicatechin does not throw definite light on the constitution of the latter.

2. Tetramethyl-acacatechin has been converted into 2-hydroxy-4,6,3′,4′-tetramethoxy-3-phenylcoumarin by a method which would have yielded 4,6,3′,4′-tetramethyl-quercetin if acacatechin had been a reduced quercetin derivative as assumed by Freudenberg.

[45] Ref. 15, p. 1153.

3. The synthesis of 2-hydroxy-4,6,3',4'-tetramethoxy-3-phenylcoumarin is described.
4. The synthesis of tetramethyl-acacatechin previously described by the author and since then contested by Freudenberg has been repeated.
5. The chroman nucleus in pentamethyl-acacatechin is shown to undergo fission by the interaction of alkali and methylating reagents when β,γ-2,4,6,3',4'-heptamethoxy-α,α-diphenylpropane is produced.
6. β,γ,2,4,6,3',4'-Heptamethoxy-α,α-diphenylpropane has been synthesized.
7. The production of the α,α-diphenylacetic acid derivatives from acacatechin is emphasized, thus showing that the α,α,-diphenylpropane structure is the normal structure of acacatechin.
8. It is shown that 2-hydroxy-4,6,3',4'-tetramethoxy-3-phenylcoumarin obtained from tetramethyl-acacatechin and 4,6,3',4'-tetra-acetoxy-3-phenylcoumarin prepared by the action of acetic anhydride on maclurin yield the same substance when reacted on with hydriodic acid.
9. These observations confirm the formula assigned to acacatechin by the author.

BRISTOL, ENGLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF OTAGO]

EXPERIMENTS ON THE SYNTHESIS OF APOFENCHOCAMPHORIC ACID. PREPARATION OF ALPHA, ALPHA-DIMETHYL-GAMMA-CARBOXYADIPIC ACID

BY KENNETH CHARLES ROBERTS

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Recent literature on the dicyclic terpenes contains several references[1] to a dibasic acid of the formula $C_9H_{14}O_4$. This acid is isomeric with apocamphoric acid, and has been named apofenchocamphoric acid. All the papers cited appear to regard it as having the constitution 4,4-dimethylcyclopentane-1,3-dicarboxylic acid but, since the constitutions of the substances from which the acid is obtained can in no case be regarded as definitely established, this tentative structure still remains to be proved. It has been the aim of the present investigation to synthesize 4,4-dimethylcyclopentane-1,3-dicarboxylic acid and thus prove, if possible, its identity with apofenchocamphoric acid.

By analogy with Perkin and Thorpe's synthesis of camphoric acid, it was thought that, if α,α-dimethyl-γ-carboxyadipic acid could be prepared, this could then be readily closed up to a five-carbon ring, and the resulting cyclic keto acid transformed into the required 4,4-dimethylcyclopentane-

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[1] Nametkin and Chuchrikovaia, *J. Chem. Soc.*, 108, 701 (1915). Komppa and Roschier, *ibid.*, 112, 398 (1917); 122, 1167 (1922). Roschier, *ibid.*, 116, 408 (1919).

1,3-dicarboxylic acid. The synthesis of α,α-dimethyl-γ-carboxyadipic acid has, therefore, been carried through, the steps being the following.

(a) Ethyl-α,α-dimethylacetone dicarboxylate was condensed by means of its monosodium derivative, with chloro-acetic ester.

$$C_2H_5OOC.C(CH_3)_2.CO.CHNa.COOC_2H_5 \longrightarrow$$
$$C_2H_5OOC.C(CH_3)_2.CO.CH\ (CH_2COOC_2H_5).COOC_2H_5$$

(b) The resulting ester was reduced, first to the corresponding hydroxy ester, and, finally, hydrolyzed and reduced to the corresponding dimethylcarboxyadipic acid, $HOOC.(CH_3)_2.CH_2.CH(CH_2.COOH).COOH$. Only a very small yield was obtained, however, and it will be necessary to prepare the acid at considerably less expense before an attempt is made to carry the synthesis further. This work is now in hand.

Experimental Part

First Condensation. Preparation of Ethyl-α,α-dimethylacetone Dicarboxylate ($C_{11}H_{18}O_5$)

The method described by Perkin and Smith[2] was adopted, namely, condensation of ethyl acetate and ethyl dimethylmalonate with powdered sodium, but it was found possible to double the yield by introducing the two following modifications. (a) Instead of ethyl acetate, a synthetic mixture of absolute alcohol and anhydrous ethyl acetate[3] was used. This was found to increase the yield by one-half. (b) A steady stream of carbon dioxide was passed through the reaction mixture. This prevented loss of ester by alkaline hydrolysis during the condensation, and resulted in a further material increase in the yield.

The above two modifications may prove to be of general applicability in increasing the efficiency of condensations of this type.

Second Condensation. Preparation of Ethyl-α,α-dimethyl-β-keto-γ-carbethoxyadipate ($C_{15}H_{24}O_7$)

$C_{11}H_{18}O_5$ (above) was converted in the usual way into its monosodium derivative, care being necessary to avoid the formation of appreciable quantities of the di-derivative. The semi-solid contents of the flask were then refluxed with a 25% excess of chloro-acetic ester until the product was no longer alkaline (three to four hours), and the ester separated in the usual way. Distillation of the residue after removal of ether, alcohol and unchanged chloro-acetic ester gave a good yield of a colorless oil which gave an intense red coloration with ferric chloride, b. p., 150–160° (14 mm.); n_D, 1.4400.

Anal. Calcd. for $C_{15}H_{24}O_7$: C, 57.0; H, 7.6. Found: C, 56.9; H, 7.8.

In one instance a small amount of the di-derivative, $C_2H_5OOC.C(CH_3)_2.CO.C(CH_2.COOC_2H_5)_2.COOC_2H_5$, giving no coloration with ferric chloride, was isolated; b. p., 170–180° (14 mm.); n_D, 1.4458.

Anal. Calcd. for $C_{19}H_{30}O_9$: C, 56.7; H, 7.5. Found: C, 56.9; H, 7.8.

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[2] Perkin and Smith, *J. Chem. Soc.*, **83**, 12 (1903).

[3] Compare *Chem. Ind.*, **43**, 295T–297T (1924).

Reduction of Ethyl-α,α-dimethyl-β-keto-γ-carbethoxyadipate in Two Stages

I. Formation of Ethyl-α,α-dimethyl-β-hydroxy-γ-carbethoxyadipate ($C_{16}H_{26}O_7$).—The reduction of the keto group to a secondary alcohol group was carried through in the ordinary way, using 4% sodium amalgam and a 1:16 solution of the ester in aqueous alcohol. To separate the ester after reduction, the liquid was freed from mercury and solid bicarbonate, neutralized with dil. hydrochloric acid, and heated on a water-bath to remove alcohol. The ester separated and was extracted with ether. The hydrolyzed portion, amounting to about 15%, was recovered from the combined residues by acidifying, evaporating nearly to dryness and extracting with ether. The sirupy hydroxy acid (or lactone?) thus recovered was added to the reduced ester, and the combined product treated as described in II.

II. Hydrolysis and Reduction to α,α-Dimethyl-γ-carboxyadipic Acid ($C_9H_{14}O_6$).—

(a) A preliminary attempt at hydrolysis and reduction of the hydroxy ester ($C_{16}H_{26}O_7$), using red phosphorus and hydriodic acid (d., 1.69), resulted in the isolation of crystals; m. p., 146°.

Neutr. eq. Calcd. for the γ-lactone, $C_9H_{12}O_6$: 108. Found: 110.5, 110.3.

Anal. Calcd. for $C_9H_{12}O_6$: C, 50.0; H, 5.56. Found: C, 50.0, 49.5; H, 5.96, 5.87.

(b) Finally, the hydroxy ester was treated with red phosphorus and fuming hydriodic acid (d., 1.93) in the cold. When the mixture had stood for some time, the ethyl iodide resulting from hydrolysis was removed, and the mixture then refluxed for nine hours. To separate the organic acid, the hydriodic acid was distilled off in a vacuum, the residue washed onto a filter with ether, the filtrate freed from iodine and water in the usual way and the ether then removed. Crystals, m. p. 139–141°, were deposited on standing in a vacuum desiccator overnight, but no solvent was found from which they could be recrystallized.

Neutr. eq. (titration with $Ba(OH)_2$. Calcd. for $C_9H_{14}O_6$: 72.7. Found: 73.2, 73.6.

Anal. Calcd. for $C_9H_{14}O_6$: C, 49.5; H, 6.4. Found: C, 49.6; H, 6.6.

The yield from this reduction was only about half of that calculated.

In conclusion, the author wishes to express his thanks to Professor J. K. H. Inglis for his kind interest in the work, and for the advice and help he has given.

DUNEDIN, NEW ZEALAND

[Contribution from the Polarimetry Section, National Bureau of Standards, United States Department of Commerce][1]

RELATIONS BETWEEN ROTATORY POWER AND STRUCTURE IN THE SUGAR GROUP. XV.[2] CONVERSION OF LACTOSE TO ANOTHER DISACCHARIDE, NEOLACTOSE. THE CHLORO-HEPTA-ACETATE AND TWO OCTA-ACETATES OF NEOLACTOSE

By Alfons Kunz and C. S. Hudson

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It was stated in a recent article[3] dealing with the revision of the rotation of α-chloro-acetyl lactose that "on one occasion, upon the addition of petroleum ether to the mother liquor of an original crystallization of α-chloro-acetyl lactose, which had been prepared from 20 g. of crude lactose octa-acetate, there slowly separated about 1 g. of a crystalline substance in the form of prisms which showed $[\alpha]_D^{25} = +71.7$ in chloroform, melted at 160° and gave a strong chlorine reaction with silver nitrate. It seems to be a new chlorine derivative of lactose octa-acetate and is being examined further." The results of this examination are now presented.

The substance proves to be a chloro-hepta-acetate of a disaccharide (di-hexose) and is thus an isomer of chloro-acetyl lactose. It has been transformed by reactions in which its chlorine atom was exchanged for the acetyl radical to two crystalline isomeric pure octa-acetates of a disaccharide, which are different from all known acetates of the sugar group. The saponification of these acetates has yielded a sirupy sugar which has not crystallized when seeded with lactose and on re-acetylation regenerates these acetates. Since no difficulty was found in preparing crystalline lactose in high yield by the saponification of lactose octa-acetate, it seems reasonably certain that the new substances are derivatives of a disaccharide that is different from lactose. The sugar will provisionally be named neolactose, pending the determination of its structure. Its identity with known disaccharides is excluded in all cases but one by the properties of its two octa-acetates. It may prove to be the 5-galactosido-mannose which Bergmann[4] prepared from the oxidation of lactal but, since acetates of 5-galactosido-mannose are not described, further experimental work will be required to decide the question whether neolactose is Bergmann's 5-galactosido-mannose.[4a]

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[1] Published by permission of the Director of the Bureau of Standards.

[2] Article XIV was published in This Journal, 48, 1434 (1926).

[3] Hudson and Kunz, *ibid.*, 47, 2052 (1925).

[4] Bergmann, *Ann.*, 434, 79 (1923).

[4a] Note added May 10, 1926. Subsequent results, which will soon be published, have shown that neolactose is different from 5-galactosido-mannose and is indeed a new sugar. It is dextrorotatory but after acid hydrolysis the solution is levorotatory, which distinguishes it definitely from 5-galactosido-mannose. The structure of neolactose has been found to be that of *d*-galactosido-*d*-altrose.

The new chlorine derivative, which will be designated *α-chloro-acetyl neolactose*, was originally obtained in low yield by Skraup and Kremann's[5] chlorination process, which consists in boiling the chloroform solution of a sugar acetate, here lactose octa-acetate, with phosphorus pentachloride and a small amount of anhydrous aluminum chloride as catalyst. A systematic study of this reaction was made in the hope of finding a way to increase the yield of chloro-acetyl neolactose and it led to a surprising result. The aluminum chloride is not only a catalytic agent with respect to the chlorination by phosphorus pentachloride but it chlorinates the octa-acetate in the absence of the pentachloride and gives the desired good yield of chloro-acetyl neolactose. It has been found as the result of numerous trials, however, that commercial sublimed aluminum chloride is not suitable for use in this case. It is necessary to employ highly reactive aluminum chloride such as is required for the Friedel-Crafts reaction. This material has been prepared by Stockhausen and Gattermann's[6] method, which consists in leading a stream of hydrogen chloride over red-hot aluminum (iron-free), and by its use chloro-acetyl neolactose has been prepared in regular and satisfactory yield. A large excess of aluminum chloride is required. It appears that the reaction involves an absorption of the lactose octa-acetate at the surface of the insoluble aluminum chloride, a conclusion which is drawn from the facts, (1) that the acetate is largely removed from the chloroform solution by the solid aluminum chloride and (2) that finely divided aluminum chloride is more reactive than coarse lumps. The solid phase in the reaction mixture goes through a series of color changes. It first becomes cherry-red, then lilac and finally dark gray. At this stage the mixture is to be cooled and shaken with ice; the dark color then disappears and the solid sugar acetate derivative of aluminum chloride decomposes to yield α-chloro-acetyl lactose and α-chloro-acetyl neolactose, which dissolve in the chloroform layer, and aluminum chloride, which dissolves in the water. When the reaction is stopped when the color is cherry-red α-chloro-acetyl lactose results in good yield (about 60%) but only a small quantity of the neolactose derivative is obtained. Evidently, α-chloro-acetyl lactose is formed first and is then transformed to the isomeric neolactose compound. This conclusion was verified by substituting α-chloro-acetyl lactose for the octa-acetate in one experiment and obtaining a normal yield of α-chloro-acetyl neolactose from it. During the chlorination reaction there is a slow decomposition and in order to obtain the best yield of the neolactose derivative the reaction must be stopped at the empirically determined stage already mentioned, which we find to result in a yield of about 30% of α-chloro-acetyl lactose and 20% of α-chloro-acetyl neolactose, based on the weight of the original lactose

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[5] Skraup and Kremann, *Monatsh.*, **22**, 375 (1901).

[6] Stockhausen and Gattermann, *Ber.*, **25**, 3521 (1892).

octa-acetate. The two substances are readily separated and purified and their physical properties (see Table I) show unmistakably that they are different substances.

TABLE I

ROTATIONS IN CHLOROFORM OF LACTOSE AND NEOLACTOSE DERIVATIVES

Substance	$[\alpha]_D^{20-6}$	$[\alpha]_{578}^{20}$	$[\alpha]_{546}^{20}$	$[\alpha]_{436}^{20}$	M. p., °C.
α-Chloro-acetyl lactose	+84	....	....	....	120
α-Chloro-acetyl neolactose	+71.2	+75.6	+84.5	+147	182
α-Octa-acetyl lactose	+53.9	....	....	....	152
α-Octa-acetyl neolactose	+53.4	+56.0	+63.1	+112	178
β-Octa-acetyl lactose	− 4.3	....	....	....	90
β-Octa-acetyl neolactose	− 7.1	− 7.9	− 9.2	− 16.2	148

α-Chloro-acetyl neolactose yielded two isomeric crystalline octa-acetates of neolactose, according to the method used in replacing the chlorine atom by the acetyl radical. When a solution of the substance in acetic anhydride was warmed on the steam-bath with silver carbonate or with sodium acetate, a good yield of a neolactose octa-acetate of $[\alpha]_D$ about +44–46 was obtained. Under like conditions α-chloro-acetyl lactose did not react with sodium acetate, and with silver carbonate it yielded β-lactose octa-acetate ($[\alpha]_D$ = —2). At the boiling point of acetic anhydride it reacted with sodium acetate to give the same octa-acetate ($[\alpha]_D$ = —4). When an acetone solution of α-chloro-acetyl neolactose was gently boiled with silver carbonate and the resulting substance, which is presumably a hepta-acetate of neolactose, was then acetylated by heating it with acetic anhydride and sodium acetate there was obtained in good yield a neolactose octa-acetate of $[\alpha]_D$ about —0.5. The low-rotating form will be designated *neolactose β-octa-acetate* and the strongly dextrorotatory form *neolactose α-octa-acetate,* in conformity with the names of the well-known α- and β-octa-acetates of lactose. In a similar manner chloro-acetyl neolactose will be designated as an alpha form because of its high dextrorotation in conformity with the previous naming of α-chloro-acetyl lactose from similar considerations.[7]

The transformations of the α-chloro-acetates of lactose and neolactose to octa-acetates by various reactions are summarized in Table II, from which it is seen that the chemical reactivities of the chloro-acetates of the two sugars are markedly different. α-Chloro-acetyl lactose yields only lactose β-octa-acetate by the reactions employed, while α-chloro-acetyl neolactose yields neolactose α-octa-acetate in most cases but its β-octa-acetate results from one of the reactions. Certainly, in the case of α-chloro-acetyl lactose or neolactose there has been realized a Walden reversal on Carbon 1 during the passage to an octa-acetate.

The molecular rotations of the carefully purified neolactose derivatives

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[7] Hudson, THIS JOURNAL, 46, 462 (1924).

TABLE II

SOME REACTIONS OF α-CHLORO-ACETYL LACTOSE AND NEOLACTOSE

Reagent and solvent	α-Chloro-acetyl lactose yields octa-acetate showing $[\alpha]_D$ as follows:	α-Chloro-acetyl neolactose yields octa-acetate showing $[\alpha]_D$ as follows:
Silver acetate in glacial acetic acid on the steam-bath	(Lactose β-octa-acetate according to literature[8])	+46.8 (Neolactose α-octa-acetate)
Silver carbonate in acetic anhydride on the steam-bath	−1.7 (Lactose β-octa-acetate)	+43.7 (Neolactose α-octa-acetate)
Sodium acetate in acetic anhydride on the steam-bath	No reaction	+46.3 (Neolactose α-octa-acetate)
Sodium acetate in acetic anhydride at boiling temperature	−3.5 (Lactose β-octa-acetate)	(Neolactose α-octa-acetate)
Silver carbonate in aqueous acetone, followed by acetylation with acetic anhydride and sodium acetate	+6.1 (Lactose β-octa-acetate)	−0.5 (Neolactose β-octa-acetate)

are recorded in Table III, and from them values of the rotations of the end asymmetric carbon atom (A_{Ac} and A_{Cl}) have been obtained in the usual way.[7] The value of A_{Ac} is normal, conforming fairly closely with the coefficient of the lactose series, which indicates that the two neolactose octa-acetates are a true α, β pair having like ring structure, though the position of the ring is unknown. The value of A_{Cl} is much smaller than that found for α-chloro-acetyl lactose. Whether this difference is to be attributed to the possession of another type of ring by α-chloro-acetyl neolactose or to other influences must be left for further investigation. Possibly the determination of the hexoses of which neolactose is composed will throw light upon this question.

TABLE III

VALUES OF THE COEFFICIENTS A_{Ac} AND A_{Cl} IN THE NEOLACTOSE SERIES

Neolactose	Mol. wt.	$[\alpha]_D$ in $CHCl_3$	$[M]_D$	Rotation of end carbon	A for corresponding derivative of lactose
α-Octa-acetyl	678	+53.4	+36,200	A_{Ac} =	19,700[9]
β-Octa-acetyl	678	− 7.1	− 4,810	+20,500	
α-Chloro-acetyl	655	+71.2	+46,700	A_{Cl} =	38,100[9]
				+31,000	

Experimental Part

Preparation of α-Chloro-acetyl Neolactose.—One hundred g. of crude lactose octa-acetate[3] was dissolved in a liter of absolute chloroform; the solution was filtered and to it 200 g. of Stockhausen and Gattermann's powdered aluminum chloride was added,

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[8] Bodart, *Monatsh.*, **23**, 5 (1902).

[9] Hudson and Dale, THIS JOURNAL, **40**, 993 (1918).

the mixture being kept at 65° during two hours in a 2-liter, round flask with a reflux condenser closed by a calcium chloride drying tube. The color changes that were observed during the progress of the reaction have been described. The aluminum chloride remains undissolved and the lactose octa-acetate, originally in the chloroform solution, disappears therefrom and unites with the solid phase (aluminum chloride). Whether it unites before or after a transformation has not been determined. The reaction mixture is next cooled, and the solution and dark colored suspended solids are poured into a 2-liter separatory funnel half filled with cracked ice. The coarse pieces of aluminum chloride remaining in the flask were not removed but were rinsed with 100 cc of chloroform, and the suspension of finer solids was poured into the funnel. The chloroform suspension was shaken thrice with ice water, during which treatment the aluminum chloride dissolved in the water while the acylated sugar compounds dissolved in the chloroform. The chloroform solution was then dried with calcium chloride and evaporated under reduced pressure to a sirup which was dissolved in 750 cc. of ether and the solution was kept in an ice box until crystallization was complete, which required about five days. The yield was 50 g. of a mixture of the α-chloro-acetates of lactose and neolactose. The crystals of the lactose compound are needles arranged in radiating clusters while those of the neolactose derivative are well formed stout prisms and the two substances are readily distinguished by the naked eye. They were easily separated by extraction with 100 cc. of cold ethyl acetate which dissolved the lactose compound but left the α-chloro-acetyl neolactose; the yield of the latter was 20 g. of crude substance. This was recrystallized by dissolving in 200 cc. of hot ethyl acetate, decolorizing with carbon and adding 200 cc. of ether; yield, 18 g. of pure α-chloro-acetyl neolactose. Another recrystallization did not change its specific rotation; m. p., 182° with decomposition; $[\alpha]_D^{25} = +71.2$ in pure chloroform (0.5115 g. of subst., 50 cc. of chloroform solution; 4.37° rotation to the right, 600-mm. tube). The chlorine percentage was 5.45 from the reaction of the substance in aqueous acetone solution with silver nitrate, 5.42 to 5.47 by C. W. Bacon's method[10] and 5.38 by the Carius method, in comparison with 5.41 calculated for a chloro-hepta-acetyl disaccharide (di-hexose), $C_{26}H_{35}O_{17}Cl$.

The acetyl determination was made by a new method which gives accurate results and is quite simple to carry out.[11] One-half g. of the substance was dissolved in 50 cc. of pure acetone, the solution was cooled in an ice-and-salt mixture, 100 cc. of 0.1 *N* aqueous potassium hydroxide solution was added drop by drop and the solution kept for two hours below 0° in the mixture. The excess alkali was then titrated with 0.2 *N* hydrochloric acid. A control test was made to determine the slight amount of alkali that is neutralized by the acetone. Measurements with chloro-acetyl lactose showed the method to be reliable; 0.5189 g. of the substance was equivalent to 31.6 cc. of 0.2 *N* hydrochloric acid in two hours' action (calculated, 31.6 cc.), and another sample after 16 hours' action still gave the calculated percentage. By this method 0.4884 g. of chloro-acetyl neolactose was found to be equivalent to 29.7 cc. of 0.2 *N* hydrochloric acid in comparison with 29.8 cc. calculated. Chloro-acetyl neolactose is very soluble in chloroform, benzene and acetone, slightly soluble in cold ethyl acetate or alcohol, but considerably so in the hot solvents, slightly soluble in ether and insoluble in petroleum ether and water. It reduces Fehling's solution on heating. It is a stable substance and can even be kept in an open bottle for long periods.

Preparation of Neolactose α-Octa-acetate.—Ten g. of α-chloro-acetyl neolactose and 10 g. of anhydrous sodium acetate were heated with 50 cc. of acetic anhydride on the steam-bath for one hour and the solution was poured into ice water. The pre-

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[10] Bacon, This Journal, 31, 49 (1909).

[11] This method was devised by Dr. Kunz (C. S. H.).

cipitated oil quickly crystallized and the yield of octa-acetate was nearly quantitative. It was decolorized with carbon and purified by recrystallization from hot alcohol. After four recrystallizations, using 300 cc. of alcohol each time, and four using 200 cc., 1.6 g. of the substance was obtained melting at 178°; $[\alpha]_D^{26} = +53.2$ *in chloroform.* The values were not appreciably changed by five additional recrystallizations, and the value $[\alpha]_D^{24} = +53.4$ (0.4626 g. of the subst., 50 cc. of chloroform solution; 2.964 degrees to the right, 600mm. tube) obtained after the thirteenth recrystallization is chosen for the value of neolactose α-octa-acetate in chloroform. The acetyl estimation was made by the previously mentioned method; 0.5725 g. of the substance was found to be equivalent to 33.5 cc. of 0.2 *N* hydrochloric acid, the reaction time being six hours, in comparison with 33.7 cc. calculated for a di-hexose octa-acetate. The substance is quite soluble in chloroform, acetone, ethyl acetate and benzene, slightly soluble in cold alcohol and insoluble in ether, petroleum ether and water. It is conveniently recrystallized from hot alcohol, 1 g. requiring about 50 cc. of solvent. On cooling, the acetate crystallized in plates grouped in star form. It reduces Fehling's solution on heating.

Preparation of Neolactose β-Octa-acetate.—A mixture of 15 g. of α-chloro-acetyl neolactose, 10 g. of freshly prepared silver carbonate, 100 cc. of pure acetone and 5 cc. of water was refluxed for one hour, filtered after the addition of a little decolorizing carbon and the filtrate evaporated to dryness under reduced pressure. The crystalline residue, which was presumably a neolactose hepta-acetate, was acetylated by heating for one-half hour on the steam-bath with 50 cc. of acetic anhydride (96%) and 5 g. of anhydrous sodium acetate. When the solution was poured into ice water a crude octa-acetate quickly crystallized in nearly quantitative yield. After two recrystallizations from 200 cc. of hot alcohol, using some decolorizing carbon in the first, 12.5 g. of the substance crystallizing in beautiful plates was obtained; $[\alpha]_D^{23} = -0.8$; m. p., 145°. It is a mixture of about 90% of the β- and 10% of the α-octa-acetate of neolactose, judging from its rotation. The freeing of the beta form from its alpha isomer required 17 recrystallizations from alcohol. The $[\alpha]_D^{26}$ value was then —7.03 in chloroform. After the nineteenth recrystallization, $[\alpha]_D^{25} = -7.16$ and the melting point 148°; and after the twenty-first, $[\alpha]_D^{23} = -7.04$ (0.5102 g. of substance, 50 cc. of pure chloroform solution; 0.431° to the left, 600mm. tube). The melting point 148° and the value $[\alpha]_D^{24} = -7.1$ *in chloroform are chosen for the pure neolactose β-octa-acetate. It is* readily soluble in chloroform, acetone, ethyl acetate and benzene, soluble in hot alcohol from which it crystallizes on cooling, only slightly soluble in ether and hot water, insoluble in petroleum ether and cold water. It reduces Fehling's solution on heating.

An acetyl estimation was made by the new method, using the previously mentioned product showing $[\alpha]_D^{23} = -0.8$; 0.5162 g. of the substance was equivalent to 30.1 cc. of 0.2 *N* hydrochloric acid; the value calculated for an octa-acetyl di-hexose is 30.4. The duration of the treatment was here six hours. In another test lasting for 16 hours the same result was obtained.

Summary

It is found that lactose octa-acetate in chloroform solution can be chlorinated with highly reactive aluminum chloride. The first product is the well known α-chloro-acetyl lactose but on longer duration of the reaction a crystalline chloro-hepta-acetate of a disaccharide isomeric with lactose, which will be designated provisionally neolactose, is obtained in about 20% yield. This α-chloro-acetyl neolactose has been transformed to an α- and a β-octa-acetate of neolactose, crystalline substances which are different from all known disaccharide octa-acetates. The difference of their molecular rotations has the normal value for an α, β pair of sugar acetates, and they have been named in accordance with this fact. The structure of neolactose and the applicability of the new chlorinating method to other sugar derivatives will be investigated.

One of the authors (A. K.) expresses his thanks to the International Education Board for a grant which enabled him to take part in this research.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE DYE LABORATORY OF THE CHEMISTRY DIVISION OF THE NATIONAL BUREAU OF STANDARDS, UNITED STATES DEPARTMENT OF COMMERCE]

THE ABSORPTION SPECTRA OF BENZENE-AZOBENZENE[1]

BY WALLACE R. BRODE

RECEIVED APRIL 17, 1926 PUBLISHED JULY 6, 1926

In the decade between 1905 and 1915 a number of workers[2] made rather extensive studies of the absorption spectra of benzene-azobenzene but during the past decade little or no work has been done on this remarkable colored compound. Benzene-azobenzene may well be considered the parent substance of all azo dyes and as such a more accurate determination of its absorption spectra should be welcome. With the development of more accurate apparatus and the general adoption of the method of relative transmission for the determination of absorption spectra, the curve for this compound can be determined with greater accuracy than was previously possible.

The results of this investigation show that the curve is not so simple as was previously thought, but that the principal band of this substance the simplest of azo dyes, is in reality composed of at least two overlapping bands. Repeated observations in various kinds of solvents have confirmed this fact beyond any doubt.

The apparatus used in making these measurements included a Hilger sector photometer and quartz spectrograph.[3] (For a detailed description of the apparatus see Ref. 4 c.) A slit 0.1 mm. wide, which was the equivalent of 2.5 *f* units at a frequency of 750 *f* and 2.0 *f* at a frequency of 1200 *f*, was used in making these observations. The unit of frequency[4c] (*f*)

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[1] Published by permission of the Director of the National Bureau of Standards of the U. S. Department of Commerce.

[2] (a) Hartley, *J. Chem. Soc.*, **51**, 152 (1887). (b) Baly and Tuck, *ibid.*, **89**, 982 (1906). (c) Tuck, *ibid.*, **91**, 449 (1907). (d) Hantzsch, *Ber.*, **42**, 2129 (1909). (e) Purvis and McCleland, *J. Chem. Soc.*, **101**, 1514 (1912). (f) Hantzsch, *Ber.*, **46**, 1537 (1913). (g) Purvis, *J. Chem. Soc.*, **105**, 590 (1914) (h) Baly and Hampson, *ibid*, **107**, 248 (1915).

[3] Placed at the author's disposal by the Colorimetry Section of the Optics Division of the National Bureau of Standards, U. S. Department of Commerce.

used in this paper represents vibrations ÷ (seconds × 10^{12}). The data obtained in this investigation are plotted in the accepted form as described in previous papers by the author and others.[4] In plotting these curves the diameter of the dots indicating the observed points is given not smaller than twice the width of the spectral region covered by the energy of a given frequency passing through the slit.

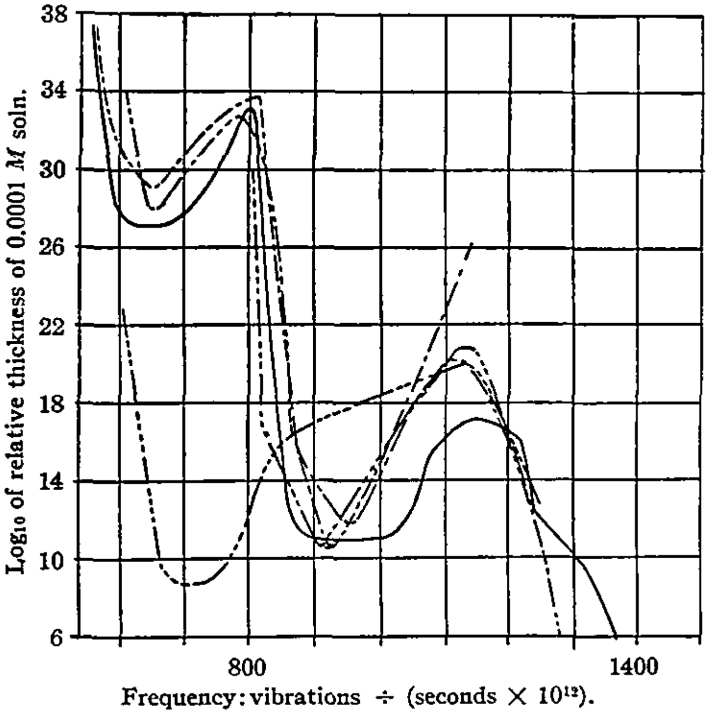

Fig. 1.—The absorption spectra of benzene-azobenzene as determined by Baly and Tuck[2b] (solid line); Baly and Hampson[2h] (one dot); Hantzsch[2d] (two dots); Purvis and McCleland[2e] (three dots) and in concd. hydrochloric acid by Tuck[2e] (four dots).

In Fig. 1 are given several of the previous determinations on benzene-azobenzene, all of which were determined by the thickness or concentration methods and not by the more accurate method of relative transmission. Since these data cannot be directly transformed into the relative transmission system it is impossible to compare these curves directly with those obtained in this work. The general shape, however, should be the same in all cases. It is to be noticed that none of these previous curves give any distinct indication of a hump on the side of the principal band (at 870 *f*) and from the straight line effects in many of them it may be assumed that the points of observation were too widely separated to show this effect.

[4] (a) Gibson and others, *J. Optical Soc. Am.*, **10**, 169 (1925). (b) Brode, *J. Phys. Chem.*, **30**, 56 (1926). (c) *Bur. Standards Sci. Paper*, **440** (1922).

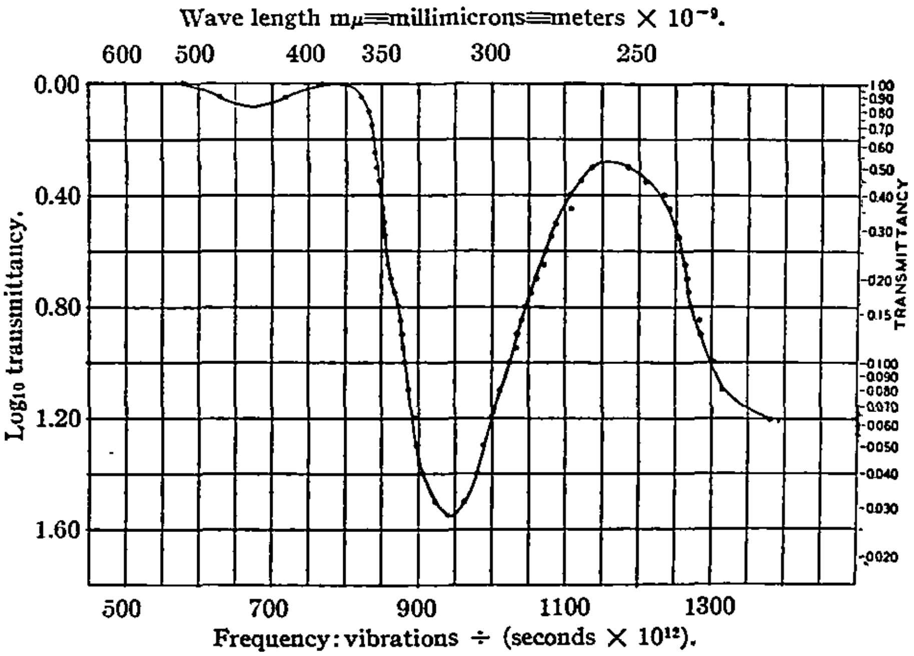

Fig. 2.—The absorption spectrum of benzene-azobenzene in ethyl alcohol (95%) concentration, 3.3 cg. per liter; cell thickness, 0.5 cm. (For numerical values see Table I).

TABLE I

THE ABSORPTION SPECTRUM OF BENZENE-AZOBENZENE IN ALCOHOL

−log₁₀ trans-mittancy	No. obs	Av. val., f	Av. dev.	Max. dev.	No. obs.	Av. val., f	Av. dev.	Max. dev.	No. obs.	Av. val., f	Av dev.	Max. dev.
0 00	6	< 580	...	...								
.05	4	630	10.0	10.0	4	720	20	30	4	824	2 0	6.0
.10	6	835	1.5	5 0	.	....	...	...	.	......	...	...
.15	1	838	...	. .	..	....	...	...	.	......	...	...
.20	5	840	0.4	1 0	.	....	...	...	.	......	...	...
.25	1	843	...	...	..	....	. .	...	.	......	...	...
.30	10	845	1.5	3.0	10	1138.4	7 0	18.0	8	1187	11 0	26 0
.35	1	848	...	. .	1	1123	...	...	1	1210	...	...
.40	6	849	1 0	2.0	6	1107.5	4.0	8.0	6	1235	4.0	7.0
.45	1	852	...	...	1	1110	...	...	1	1242	. .	..
.50	5	855	1.0	2 0	5	1088	5.0	9 0	5	1250	2.0	6 0
.55	2	856.5	0.5	0 5	2	1083 5	0.5	0.5	2	1256.5	1.5	1.5
.60	11	859.4	1 0	4.5	11	1075.5	4.0	6.5	9	1259 5	2.5	5.5
.65	1	860	...	...	1	1071	...	...	1	1264	...	...
.70	6	865.3	2.0	3.7	6	1061	3.0	4.0	6	1266	3.0	4.0
75	1	870	...	...	1	1054	...	...	1	1270	...	..
80	6	875.3	1.0	2.7	6	1046	3.0	6.0	6	1273	3.0	3.0
.85	1	877	...	...	1	1043	...	...	1	1285	...	...
90	6	880.6	1 0	2.4	6	1035.5	2.5	3 5	5	1287	5.0	11.0
.95	1	881	. .	. .	1	1036	.	...	0	......	. .	...
1 00	11	885.3	1.0	2.7	11	1026	3.5	7.0	7	1306	7.0	16.0
1.10	4	889.8	0.2	0 8	4	1013	. 3.0	5.0	1	1325	...	...
1 20	4	898 5	0.8	1.5	4	1000 5	3.0	7.5	1	> 1380	...	...
1.30	4	900	0.2	1.0	4	990	4.0	6.0	.	......	...	...
1 40	7	908	4 0	9.0	7	981	4.0	7 0	.	......	...	...
1 50	12	927	7.0	17.0	12	965	8.0	15 0	.	......	...	...

Concentration, 3 3 cg. dissolved in 95% alcohol; cell thickness, 0.5 cm.

In Fig. 2 is given the average curve as determined by a number of separate observations on the alcoholic solution of benzene-azobenzene. These determinations were made on three samples from different sources, all of which melted between 68° and 69°. The points plotted in the graph are those of the mean values of several observations as given in Table I. There is no doubt as to the existence of the side band on the left of the principal band (at 870 *f*) as shown by the results obtained. In addition to the observations recorded in Table I a large number of measurements were made at other concentrations and thicknesses and it was found that Beer's law (that the $\log_{10}$ transmittancy is directly proportionate to the concentration and thickness) holds for this dye for the concentrations studied (3.3 to 0.4 cg. per liter), confirming the data of Macbeth and Maxwell[5] on this dye. The position of the principal absorption band of this dye, as determined by 22 separate observations was found to be at a frequency of $947 \pm 2f$ ($\lambda = 316 m\mu$; $1/\lambda = 316 \times 10^{-5}$).

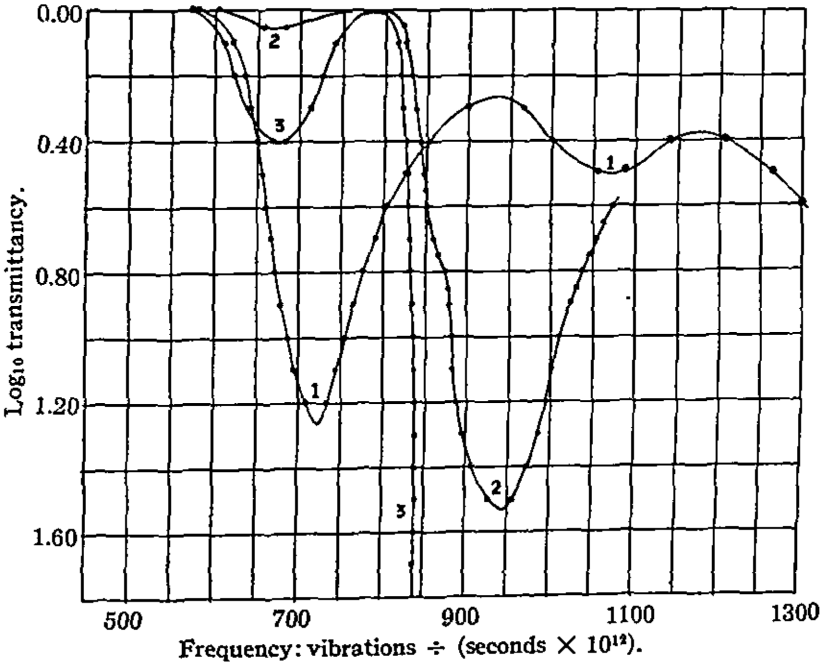

Fig. 3.—The absorption spectra of benzene-azobenzene in concd. hydrochloric acid; concentration, 1.65 cg. per liter (Curve 1); in ligroin of concentration 3.3 cg. per liter, (Curve 2), and in ligroin of concentration, 26.4 cg. per liter (Curve 3). The cell thickness in all cases is 0.5 cm.

In Fig. 3 are given the curves for benzene-azobenzene in ligroin (Curve 2) and in hydrochloric acid (Curve 1). The absorption spectrum of benzene-azobenzene in a benzene solution was also determined and found to be practically identical with the absorption spectrum in ligroin. There

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[5] Macbeth and Maxwell, *J. Chem. Soc.*, **123**, 370 (1923).

was no extensive shift of the center of the band with different organic solvents, although such a shift was shown to occur with benzene-azophenol.[4b] On this same graph is also given the curve for eight times the original concentration in ligroin (Curve 3), showing the exact position and strength of the first weak band. In the absorption curve of the entire band, this first band appears so weak that some observers have missed it entirely.

Summary

1. The absorption spectra of benzene-azobenzene have been determined in a number of solvents, and there has been shown to be no extensive shift of the band with a change of typical organic solvents as was the case with benzene-azophenol.

2. It has been shown that the absorption band of benzene-azobenzene is not simple but consists of a smaller band on the lower frequency side of the principal band which adds to the principal band to produce the observed absorption curve.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF LOUISVILLE]

THE SYNTHESIS OF ACRIDINE-9-ETHYLAMINE

BY H. JENSEN AND L. HOWLAND[1]

RECEIVED APRIL 21, 1926 PUBLISHED JULY 6, 1926

Introduction

Among the alkaloids, strychnine and brucine,[2] as well as among the valuable pharmaceutical products, acriflavine and rivanol[3] are found acridine derivatives, and therefore this group of substances, about which only little is known, has gained new interest for the chemist.

For this reason one of the authors has undertaken a series of investigations on acridine derivatives. In this paper we shall report about the preparation of acridine-9-ethylamine.

Acridine itself has antiseptic properties, and it was thought that by introducing an ethylamine side chain the optimum effect would be obtained. In the pharmaceutical investigations of the amino-alkyl bases of the phenols and of the iminazoles it has been found that the carbon skeleton giving optimum sympathomimetic activity consists of a benzene-iminazole

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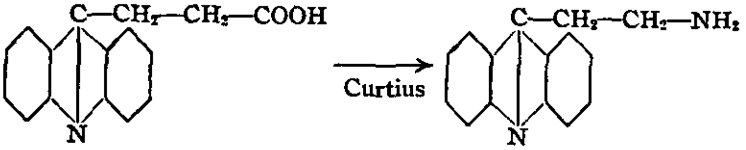
[1] This paper is an abstract of a part of a thesis presented by Louis Howland in partial fulfilment of the requirements for the degree of Master of Science in Chemistry at the University of Louisville.

[2] Perkin and Robinson, *J. Chem. Soc.*, 97, 305 (1910).

[3] For the physiological effect of these compounds, see E. Laqueur, "Die neueren chemotherapeutischen Praeparate aus der Chinin- und aus der Akridinreihe," Julius Springer, Berlin, 1923.

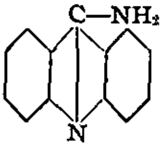
ring with a side chain of two carbon atoms, the terminal one bearing the amino group.[4]

For this reason we have chosen bases of this type in the acridine series also and first of all acridine-9-ethylamine. For the preparation of this compound acridine-9-propionic acid I, which is already known, was converted by successive steps into the ester, hydrazide, azide and the urethan and the latter by boiling with concd. hydrochloric acid into the desired acridine-9-ethylamine II.

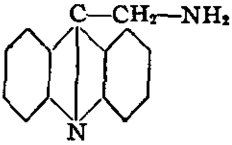


I II

Further experiments in the preparation of 9-amino-acridine III and acridine-9-methylamine IV are in progress in order that their physiological effects may be compared with that of acridine-9-ethylamine.



III



IV

Experimental Part

Preparation of Acridine-9-propionic Acid.[5]—The method of Volpi has been changed to some extent; 36 g. of succinic acid, 80 g. of diphenylamine and 90 g. of zinc chloride are heated together for eight hours at 190–200°. The melt is extracted first with a 50% sodium carbonate solution in order to decompose the zinc chloride and then with a 10% solution of sodium carbonate. By acidifying the different filtrates faintly with acetic acid, the acridine propionic acid precipitates as a fine, yellow powder. The acid is purified by re-dissolving in sodium carbonate solution and precipitating with acetic acid.

Methyl Acridine-9-propionate.[6]—Ten g. of acridine-9-propionic acid is refluxed for five hours with 150 g. of a 6% solution of hydrogen chloride in methyl alcohol. The main part of the alcohol is distilled, the remaining alcoholic solution is diluted with water, made alkaline with sodium carbonate and the ester shaken out with ether. The ether solution is dried with sodium sulfate and the ether distilled; the ester remains as an oil and is purified from petroleum ether; m. p., 95°.

Hydrazide of the Acridine-9-propionic Acid.—Ten g. of methyl acridine-9-propionate is heated with 2.5 g. of hydrazine hydrate during ten hours on the water-bath under a reflux condenser; the excess of hydrazine is then driven off and the hydrazide

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[4] Pyman, *J. Chem. Soc.*, **111**, 1124 (1917).

[5] Volpi, *Ber.*, **25**, R. 940 (1892).

[6] Schenck, *Ber.*, **39**, 2425 (1906).

remains as a solid, crystalline cake. The hydrazide is purified from ethyl alcohol, separating in stout, white needles; m. p., 205–206°. It is insoluble in water and ether and difficultly soluble in alcohol and benzene.

Anal. Calcd. for $C_{16}H_{15}N_3O$: C, 72.45; H, 5.66. Found: C, 72.64; H, 5.87.

HYDROCHLORIDE.—This precipitates from absolute alcohol in yellow needles, which decompose at 270°.

Anal. Calcd. for $C_{16}H_{15}N_3O.2HCl$: Cl, 21.00. Found: 20.80.

Acridine-urethan.—To a solution of 5.3 g. of hydrazide in 50 cc. of absolute alcohol is added 2.6 g. of amyl nitrite dissolved in 15 cc. of absolute alcohol and then a solution of 0.8 g. of hydrogen chloride in 10 cc. of absolute alcohol is gradually added, with cooling. The solution is set aside for 12 hours and then boiled for eight hours under a reflux condenser, when a lively evolution of nitrogen takes place. The main part of the alcohol is distilled and the rest diluted with water and made alkaline with sodium carbonate. The urethan separates and is purified by crystallization from carbon tetrachloride. It then forms fine, faintly yellow needles; m. p., 144–145°. It is insoluble in water, difficultly soluble in carbon tetrachloride and petroleum ether and soluble in alcohol and ether.

Anal. Calcd. for $C_{18}H_{18}N_2O_2$: C, 73.47; H, 6.12. Found: C, 73.4; H, 6.53.

HYDROCHLORIDE.—This separates from alcohol in yellow needles which decompose at 217–218°.

Anal. Calcd. for $C_{18}H_{18}N_2O_2.HCl$: Cl, 10.71. Found: 10.65.

PICRATE.—This is prepared in alcoholic solution and purified by crystallization from alcohol, forming needles; m. p., 195°.

Anal. Calcd. for $C_{18}H_{18}N_2O_2.C_6H_3N_3O_7$: C, 55.07; H, 4.02. Found: C, 54.88; H, 4.29.

Acridine-9-ethylamine.—Five g. of urethan is heated with 150 cc. of concd. hydrochloric acid for seven hours under a reflux condenser. The main part of the acid is then evaporated on the water-bath. By cooling the solution the greater part of the dihydrochloride precipitates. The salt is purified by crystallization from absolute alcohol; it precipitates in fine, yellow needles which contain one molecule of water of crystallization and decompose between 225° and 230°. It is very easily soluble in water and difficultly soluble in absolute alcohol and ether.

Anal. Calcd. for $C_{15}H_{14}N_2.2HCl.H_2O$: Cl, 22.80. Found: 22.73, 22.70.

BENZOYL DERIVATIVE.—By shaking the acridyl-ethylamine dihydrochloride with benzoyl chloride in 10% sodium hydroxide solution the benzoyl derivative is formed; it separates from alcohol in white needles; m. p., 213°.

Anal. Calcd. for $C_{22}H_{18}N_2O$: C, 81.00; H, 5.52. Found: C, 81.33; H, 5.87.

PICRATE.—This is prepared in alcoholic solution, then forming short, yellow needles; m. p., 225°.

In order to obtain the free base, the dihydrochloride is dissolved in water and aqueous ammonia is added. The free base precipitates in silky leaves; m. p., 145°.

In the air or in the vacuum desiccator the substance turns red.

Summary

Acridine-9-ethyl amine has been prepared from acridine-9-propionic acid by successive formation of the ester, the hydrazide, the azide, the urethan and finally the ethylamine.

LOUISVILLE, KENTUCKY

[Contribution from the Department of Chemistry, Yale University]

THE CATALYTIC DECOMPOSITION OF SIMPLE GLYCERIDES

By F. L. Simons[1]

Received April 24, 1926 Published July 6, 1926

In an attempt to open up our natural supplies of glycerides to further industrial use, Mailhe[2] adopted catalytic decomposition as his line of attack. He succeeded in preparing from a number of oils (cottonseed, rape, colza castor, etc.) a 20 to 30% yield of motor spirit, consisting of benzene, toluene, hexanes and other hydrocarbons. His process consisted essentially of a preliminary cracking of the glyceride over a copper-magnesia or copper-alumina catalyst, followed by hydrogenation of the low-boiling fraction of the product over nickel. Mailhe's work has been largely empirical, of course, as the high temperatures employed (600–650°) resulted in too profound a decomposition to justify any speculation as to reaction mechanism.

Our present knowledge of the behavior of glycerides at high temperatures is very meager. A review of the literature brings to light, outside of Mailhe's work, only a few scattered researches, such as those of Bussy,[3] Tilley[4] and Krafft[5] on the distillation of castor oil. Straight catalytic breakdown of a series of simpler glycerides seems to have been untried, although such research would be very useful in laying a foundation for future work along this line with the more complex natural compounds. It is, therefore, the purpose of this paper to present some of the results observed in the decomposition of triacetin and tripropionin over a thorium oxide catalyst, as a first step in the accumulation of systematic data for this series of glycerides.

Discussion

What to expect from the catalytic decomposition of even the simplest glycerides is largely a matter for conjecture. Acrolein, gaseous products, the glyceride acids and higher condensation products would probably be formed. By analogy with the esters of monohydric alcohols, we might also expect the ketone corresponding to the glyceride acid. Regarding the reactions that take place at elevated temperatures (over 600°), predictions are, of course, practically impossible. The data for the four runs thus far studied (given in Table I) show that these general expectations are fulfilled.

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[1] Constructed from a dissertation presented by F. L. Simons to the Faculty of the Graduate School of Yale University in June, 1923, in partial fulfilment of the requirements for the Degree of Doctor of Philosophy (T. B. Johnson).

[2] Mailhe, *Bull. soc. chim.*, **31**, 249 (1922), and later articles.

[3] Bussy, *Ann.*, **60**, 246 (1846).

[4] Tilley, *Ann.*, **67**, 105 (1848).

[5] Krafft, *Ber.*, **10**, 2034 (1877).

TABLE I

SUMMARY OF EXPERIMENTAL RESULTS

Run number	1	2	3	4
Glyceride	Triacetin		Tripropionin	
Temperature, °C.	460	525	420	510
Quantity used, g.	140	191.5	121	126.5
Liquid product, g.	97	134.5	98	78
Gases evolved, liters	16	21	11	31
PERCENTAGE COMPOSITION OF LIQUID PRODUCT				
Acrolein	21.0	14.1	4.0	6 7
Allyl alcohol	?	?	4.0	5 3
Crotonaldehyde	...	2.6	6 2	10.6
Water	...	?	?	6.6
Formic acid	7.0	20.0	...	...
Acetic acid	27.4	25.0	14.5	10.6
Propionic acid	...	...	17.5	33.5
Diacetin	24.2	?	...	...
Triacetin	4.6	...	...	...
Tripropionin	...	...	47.8	9.5
Tarry materials	10.1	30.6	4.0	13.3
PERCENTAGE COMPOSITION OF GASEOUS PRODUCT				
CO	not	36.6	34.9	18.5
CO_2	deter-	34.1	37.3	53.3
C_nH_{2n}	mined	13.0	8.2	9.0
H_2		6.8	10.7	17.2
C_nH_{2n+2}		present	present	present

It will be noted that decomposition of either glyceride is not complete unless the temperature is considerably over 500°. Preliminary trials also showed that decomposition does not begin, or rather does not take place to any great extent, until approximately 380° is reached. It is also notable that tripropionin is broken down at a slightly lower temperature than triacetin.

As might be expected, large amounts of tarry materials are formed, especially at the higher temperatures. Those runs that show unchanged glyceride in the product, show less tar than the others, and *vice versa.* Considerable amounts of this tar remained in the packing of the reaction tube at the end of each run. It had the general appearance of a very soft pitch, was insoluble in alcohol and soluble in benzene. It was not subjected to any study.

Careful search failed to reveal the presence of any dipropionin in the products from Runs 3 and 4. This is rather curious on the whole, and leads to the conclusion that under the particular conditions involved the triglyceride is more stable than the diglyceride. In the runs with triacetin, the contrary seems to be true.

Two quite unexpected substances appear in the products of decomposition, namely, the lower homolog of the glyceride acid, and hydrogen.

Formic acid appears in Runs 1 and 2, and acetic acid in Runs 3 and 4, in all cases in substantial quantities. Probably hydrogen is a product in Run 1, as well as in the others, although the gases unfortunately were not analyzed in this case. Whether or not the production of these substances is typical of all such decompositions remains to be seen.

It seems doubtful whether any particular significance is to be attached to the presence of allyl alcohol and crotonaldehyde in the products, although from the value for crotonaldehyde in Run 4 we might judge that its production was favored by higher temperatures. The water produced in Run 4 seems to indicate a considerable stability for tripropionin toward hydrolytic agents. This is also true in the case of hydrolysis with aqueous alkali, as far more drastic conditions are required for tripropionin than for triacetin.

Present theories of catalysis, or analogies with other known reactions seem quite inadequate to account for the fact that triacetin is decomposed into a product containing 10% of the weight of the glyceride as formic acid. The presence of hydrogen is similarly unaccounted for, although when formic acid is present, it may proceed from its decomposition.

However, two steps in these decompositions may be traced with some degree of plausibility. The first is a complete breakdown of a portion of the glyceride which liberates water and a variety of other products. The débris of the glycerol chain appears as acrolein, and some of the glyceride acid is set free as such. At the higher temperatures, this profound decomposition predominates, as would be expected. The second step is probably a simple hydrolysis of other portions of the glyceride through the agency of water previously formed, whereby the acid and a lower glyceride are produced. The results for triacetin indicate the truth of this and, although lower homologs do not appear in the runs with tripropionin, the high acid content points in this direction. The mode of formation of formic acid and other products may be made clear only by further work with other members of the series and with mixed glycerides.

Experimental Part

The glycerides used in the work were prepared with special care, the method for triacetin being straight acetylation of glycerol with acetic anhydride and sodium acetate, and for tripropionin, simple refluxing of pure propionic acid with dry glycerol in the presence of anhydrous potassium bisulfate at 110° for 60 hours.

Curiously enough, tripropionin is not reported in the literature. The product obtained boiled at 130–132° (3 mm.); attempts to distil at pressures above 20 mm. resulted in partial decomposition. The material is a colorless and practically odorless liquid, less mobile than triacetin, but slightly soluble in water, and very slow to hydrolyze with aqueous alkali; d_{18}^{20}, 1.100; n_{D}^{15}, 1.434.

Anal. Subs.: 1.0114, 1.0013: 17.42, 17.14 cc. of 0.6719 *N* NaOH used on hydrolysis. Calcd. for $(CH_2OCOC_2H_5)_2CHOCOC_2H_5$: NaOH equiv.: 0.4682, 0.4607. *Found*: 0.4669, 0.4621.

The method employed in the decompositions was a simple one, consisting essentially of a means of dropping the glyceride directly onto the heated catalyst, with suitable provision for condensing and collecting the gaseous and liquid products. The catalyst in all cases was thorium oxide, prepared by ignition of the nitrate, and supported on finely cracked, porous tile. The reaction chamber, containing the catalyst, was a vertical silica tube, 76 by 3.8 cm., electrically heated. Analysis of the liquid products presented considerable difficulty, but the results are believed to be reasonably accurate. The determination of fatty acids was greatly facilitated by the use of their benzyl pseudothio-urea salts, a method suggested by the paper of Johnson and Donleavy.[6] The results for the four runs thus far completed have been given under the discussion.

Summary

1. The catalytic decomposition of triacetin and of tripropionin over thorium oxide has been studied at a maximum temperature of 525°.

2. Acrolein, acids, oxides of carbon, hydrocarbons and tarry condensation compounds are uniform products of decomposition. Unexpectedly, hydrogen and the lower homolog of the glyceride acid are also formed.

3. The production of the latter substances makes it impossible at present to deduce a reaction mechanism.

4. Tripropionin, prepared for this work, is a new representative of the glyceride series.

Brown University
Providence, Rhode Island

[Contribution from the Baker Chemical and the Rockefeller Physical Laboratories of Cornell University]

THE ABSORPTION SPECTRA OF PHENOLPHTHALEIN, ISOPHENOLPHTHALEIN AND OF DIPHENYLPHTHALIDE[1,2]

By W. R. Orndorff, R. C. Gibbs and S. Alice McNulty[3]

Received May 10, 1926 Published July 6, 1926

Much of the work reported on the absorption spectra of phenolphthalein has been done with alkaline solutions and in the visible region only.[4] R. Meyer and O. Fischer[5] have reported on the ultraviolet absorption of

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[6] Reported at the New Haven Meeting of the American Chemical Society, April, 1923.

[1] The assistance of a grant made to the first two authors from the Heckscher Research Foundation of Cornell University which enabled them to make the measurements described in this report is gratefully acknowledged.

[2] For a preliminary report on the absorption of phenolphthalein and isophenolphthalein, see This Journal, **46**, 2483 (1924). In that report the frequency numbers should be divided by 10, to conform with the unit used in the present article.

[3] Heckscher Research Assistant in Physics and Chemistry, Cornell University, 1921–1923. (Now Mrs. H. F. Vieweg.)

[4] Vogel, "Praktisches Spectralanal," **1889**. Formánek and Grandmougin, "Untersuch. Nachweis Farbstoffe," **1908**, vol. I, p. 129. Meyer and Marx, *Ber.*, **40**, 3603 (1907); **41**, 2446 (1908). Formánek and Knop, *Z. anal. Chem.*, **56**, 273 (1917).

[5] Meyer and Fischer, *Ber.*, **44**, 1944 (1911); **46**, 70 (1913).

the sodium salt in water and of solutions of phenolphthalein in concd. sodium hydroxide solution and in concd. sulfuric acid. In the colorless sodium hydroxide solution they found no bands while we find two. In concd. sulfuric acid they reported two bands where we find five. Howe and Gibson[6] have published some work on the ultraviolet absorption of phenolphthalein in neutral alcohol and in colored alcoholic and aqueous potassium hydroxide solutions. Their results on the first two solutions check roughly with ours except that we have found an additional band in the extreme ultraviolet in the alcoholic solution of potassium hydroxide.

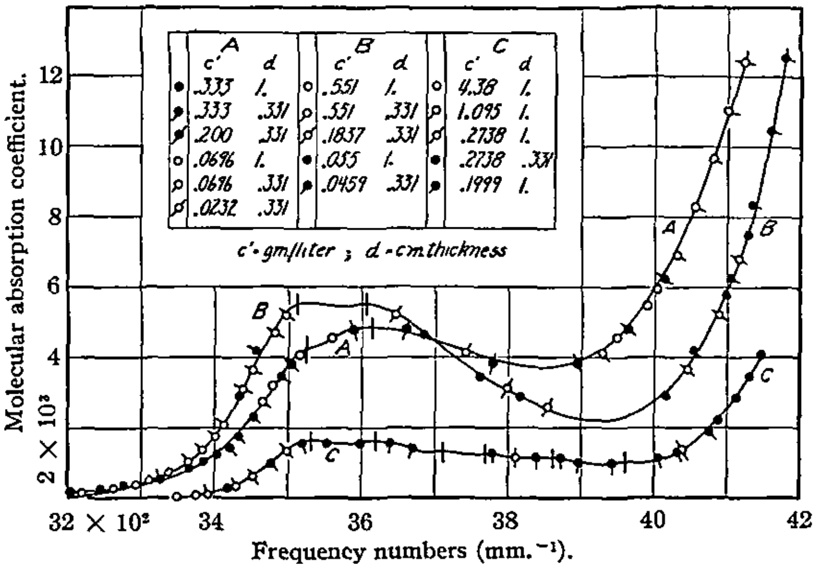

Fig. 1.—Neutral absolute alcohol solution. *A*. Phenolphthalein. *B*. Isophenolphthalein. *C*. Diphenylphthalide.

Moir[7] has reported on the absorption of a compound which he thought was *o*,*p*-dihydroxy-diphenylphthalide (our isophenolphthalein) in aqueous sodium hydroxide solution and in concd. sulfuric acid, but it is extremely doubtful, from his method of preparation, whether he really had that substance. Moreover, his data for the visible band in concd. sulfuric acid does not check with ours. Pratt[8] has studied the absorption of diphenylphthalide in neutral alcohol and in concd. sulfuric acid. He found only one band in the alcoholic solution, while we find six. He also reports three bands in concd. sulfuric acid, while we find four.

Our experimental procedure has been described in a previous article.[9] Fig. 1 shows the absorption curves of phenolphthalein (di-*p*-dihydroxy-diphenylphthalide), isophenolphthalein (*o*,*p*-dihydroxy-diphenylphthalide)

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[6] Howe and Gibson, *Phys. Rev.*, **10**, 767 (1917).

[7] Moir, *Trans. Roy. Soc. So. Africa*, **7**, 111 (1918).

[8] Pratt, *Philippine J. Science*, **8A**, 399 (1913).

[9] THIS JOURNAL, **47**, 2767 (1925).

and diphenylphthalide in neutral absolute alcohol. Diphenylphthalide, Curve C, shows six bands in the ultraviolet, the first two of which at frequency numbers 3531 and 3620 correspond to the two bands for phenolphthalein, Curve A, at 3523 and 3613 and for isophenolphthalein, Curve B, at 3511 and 3606. It is interesting to note that while for diphenylphthalide and isophenolphthalein these two bands have equal intensities, in phenolphthalein the band at 3523 has a lower intensity than the one at 3613. The introduction of the two hydroxyl groups into the molecule of diphenylphthalide has markedly increased the intensity of absorption and at the same time has suppressed the weaker bands in the further ultraviolet. Benzaurin[9] and di-*p*-dihydroxy-triphenylmethane[9] in neutral alcoholic solution both show two bands in the same region as the two mentioned above for phenolphthalein, isophenolphthalein and diphenylphthalide.

Substance	1st band	2nd band	Difference
Phenolphthalein	3523	3613	90
Isophenolphthalein	3511	3606	95
Diphenylphthalide	3531	3620	89
Benzaurin	3526	3630	104
Benzaurin, faded	3520	3613	93
Di-*p*-dihydroxy-triphenylmethane	3465	3571	106

Di-*p*-dihydroxy-triphenylmethane also shows three more bands in the further ultraviolet comparable with three of the remaining four bands of diphenylphthalide.

Diphenylphthalide	3711	3769	3861	3960
Di-*p*-dihydroxy-triphenylmethane	3695	3782	3877	....

Fig. 2 shows the absorption curves for phenolphthalein, isophenolphthalein and diphenylphthalide in concd. sulfuric acid (93%). Diphenylphthalide, which gives a yellow solution in concd. sulfuric acid, shows two prominent bands (Curve C), one at either end of the spectrum, a phenomenon characteristic of the triphenylmethane derivatives, such as benzaurin,[9] *o*-cresol benzein, aurin, triphenylcarbinol, fuchsone and *o*-cresolsulfonephthalein[10] in this solvent. Fluorescein, sulfonefluorescein[10] and resorcinol-benzein[11] show the same phenomenon, except that the band in the extreme ultraviolet is resolved into two components.

The color of the freshly prepared sulfuric acid solutions of phenolphthalein and isophenolphthalein is due to the formation of quinoid sulfates. With these phthaleins, however, difficulties were encountered because of the progressive sulfonation of the substances in the cold, sulfuric acid solution. This is apparent from the color of the solutions—both are a deep *red* at the moment of forming the solution, but fade shortly, the phenolphthalein solution becoming *deep orange*, while the isophenol-

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[10] Unpublished data.

[11] THIS JOURNAL, 48, 1327 (1926).

phthalein solution changes rapidly to a pale *yellow*. In both cases in order to obtain consistent results, it was necessary to wait until equilibrium had been established and no further fading took place. In the case of phenolphthalein, one day was sufficient while for the isophenolphthalein, probably due to the greater degree of sulfonation, three to four days were required to reach complete equilibrium. The spectra of these *faded* solutions are shown in Curve A for phenolphthalein and in Curve B for isophenolphthalein. In the visible and near ultraviolet these two substances yield strikingly different results, the absorption of phenolphthalein being 120 times as intense as that of isophenolphthalein in the region of the band at 2025. Further in the ultraviolet the absorption becomes very similar for both substances. An attempt was made to measure the visible absorption of a fresh (*deep-red*) solution of isophenolphthalein. By working very rapidly, immediately after the material had gone into solution, data were obtained showing a molecular absorption coefficient of about 18 × 10^3 in the region of frequency number 2200, this value being about 60 times as great as that shown on Curve B for the solution which had reached equilibrium. However, even this provisional value is too low, as fading was taking place during the short interval of time necessary to fill the cell and make the measurement.

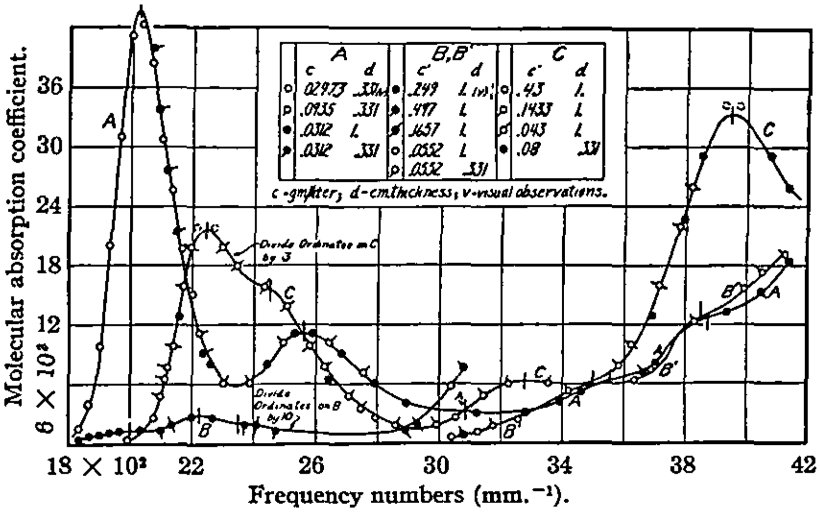

Fig. 2.—Concentrated (93%) sulfuric acid solution. *A*. Phenolphthalein. *B*, *B'*. Isophenolphthalein. *C*. Diphenylphthalide.

An attempt was made to measure the absorption of alcoholic solutions of phenolphthalein and isophenolphthalein containing various amounts of hydrogen chloride gas, but the plates obtained showed that no reaction had occurred as the absorption was exactly the same as that of the neutral solutions of the phthalein in alcohol, even with the addition of hydrochloric acid in the ratio of 11,500 molecules to one of the phthalein. This agrees with the observation of K. Meyer and Hantzsch[12] who found that phenolphthalein takes up hydrochloric acid at —30°, turning red, but on warming, all the hydrogen chloride splits off, leaving the phenolphthalein colorless.

Fig. 3 shows the effect of adding various amounts of potassium hydroxide to the alcoholic solution of phenolphthalein. Curve A for 23 molecules of potassium hydroxide shows the development of two new bands at 1785 and 2730 due to the formation of the di-potassium salt. On diluting the solution with alcohol, in order to obtain the further ultraviolet spectrum, the absorption gradually reverted to the neutral type of absorption (Curves A′ and A″), the bands at 3523 and 3625 corresponding in intensity and position to the neutral bands at 3523 and 3613. In other words, the solution at this dilution consists almost entirely of free phenolphthalein and free potassium hydroxide. On increasing the ratio of potassium hydroxide to 232 molecules (Curve B) the two bands at 1785 and 2730 have increased in intensity while in the extreme ultraviolet a new band has appeared at 3950 together with a broad shoulder at 3400. These two new bands correspond to those found in the colorless 33% aqueous potassium hydroxide solution of phenolphthalein (see Fig. 5). With this higher ratio of potassium hydroxide, an even greater dilution with alcohol failed to bring about the type of reversion noted above. A similar behavior was noted in hydrochloric acid solutions of resorcinol-benzein.[11] In the visible there is evidence of fading with time (see tailed, solid circles) due to the slow formation of the colorless tripotassium salt of the carbinol-carboxylic acid at this concentration of potassium hydroxide.

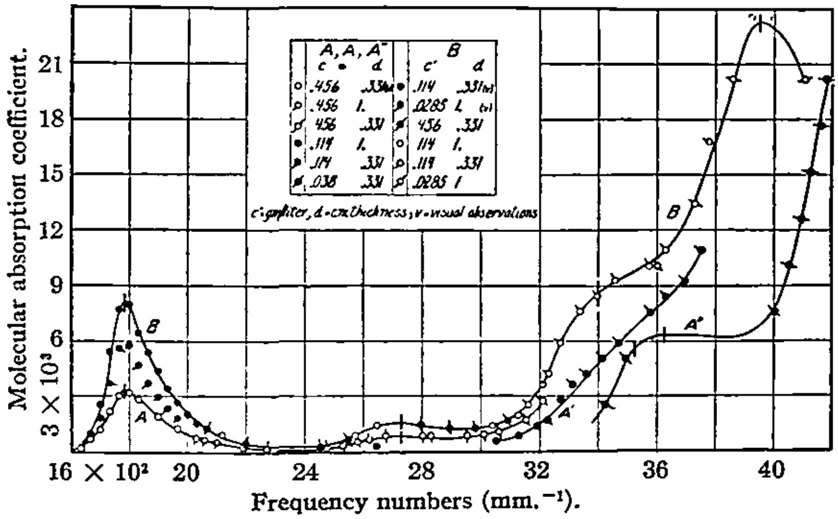

Fig. 3.—Phenolphthalein in alc. KOH. *A*, *A′*, *A″*. 23 molecules KOH:1 Phenolphthalein. *B*. 232 molecules KOH:1 Phenolphthalein.

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[12] Meyer and Hantzsch, *Ber.*, 40, 3479 (1907).

Fig. 4 shows the effect of adding varying amounts of potassium hydroxide to an alcoholic solution of isophenolphthalein. On adding two molecules of potassium hydroxide the solution is a pale *yellow* with a very weak absorption in the blue and near ultraviolet. On adding 23 molecules of potassium hydroxide the color changes to green and Curve A represents the absorption with weak bands at 1695, 2525 and 2855. On diluting this solution with alcohol the absorption reverts to the neutral type (Curves A′ and A″), the bands at 3525 and 3615 on A″ being similar in position and intensity to the bands at 3511 and 3606 for the neutral solution of isophenolphthalein. The addition of 171 molecules of potassium hydroxide produces a blue solution with the absorption bands at 1695, 2440, 3400 and 4060, the last two bands being broad shoulders which correspond in position with the two bands in the colorless solution of isophenolphthalein in 33% aqueous potassium hydroxide at 3400 and 4115 (see Fig. 5). As in the case of phenolphthalein, a greater dilution with alcohol can be made for this higher ratio of potassium hydroxide without bringing about reversion to the neutral type of absorption. Since the monosodium salt of isophenolphthalein is *yellow* and the disodium salt is *blue*,[2] while the sodium salts of phenolphthalein are red we are inclined to think that the salts of isophenolphthalein have an *o*-quinoid structure[2] while those of phenolphthalein are *p*-quinoid. This probably is the explanation of the difference in the absorption spectra of the two substances in alkaline solution.

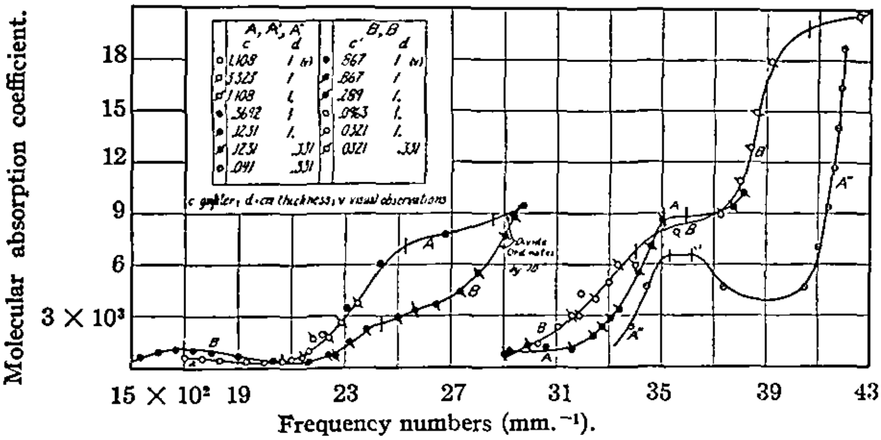

Fig. 4.—Isophenolphthalein in alc. KOH. *A, A′, A″*. 23 molecules KOH:1 Isophenolphthalein. *B, B′*. 171 molecules KOH: 1 Isophenolphthalein.

Benzaurin[9] in alcoholic potassium hydroxide solution (60 molecules of potassium hydroxide: 1 of benzaurin) shows bands analogous to those reported above for phenolphthalein with 232 molecules of potassium hydroxide and for isophenolphthalein with 171 molecules of potassium hydroxide.

	Bands at			
Phenolphthalein and 232 molecules of KOH	1785	2730	3400	3950
Isophenolphthalein and 171 molecules of KOH	1695	2440	3400	4060
Benzaurin and 60 molecules of KOH	1765	2640	3380	4005

The bands at 3380 and 4005 for benzaurin with 60 molecules of potassium hydroxide correspond with the bands at 3380 and 4050 for benzaurin in 33% aqueous potassium hydroxide solution. This is the same relationship that we noted above for phenolphthalein and isophenolphthalein in these two solvents.

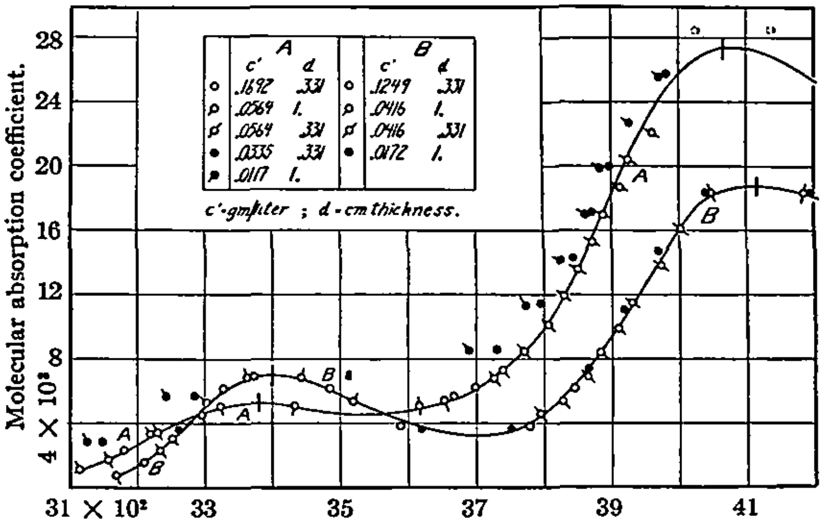

Fig. 5.—33% KOH solution. *A*. Phenolphthalein. *B*. Isophenolphthalein.

Fig. 5 shows the absorption curves for phenolphthalein and isophenolphthalein in 33% aqueous potassium hydroxide. Both substances give colorless solutions in this concentration of the potassium hydroxide. Phenolphthalein (Curve A) shows two prominent bands at 3380 and 4065. On diluting this solution with 33% potassium hydroxide in order to measure the extreme ultraviolet, the absorption tends to increase somewhat, as indicated by the solid black circles. This may be due to the formation of more of the tripotassium salt of the carbinol-carboxylic acid caused by the relatively greater concentration of the potassium hydroxide. Curve B for isophenolphthalein also shows two bands at 3400 and 4115, while the effect produced by the addition of more potassium hydroxide solution is much less pronounced, although still perceptible. Benzaurin[9] shows three bands in 33% aqueous potassium hydroxide solution, the latter two corresponding to those of phenolphthalein and isophenolphthalein.

Phenolphthalein	....	3380	4065
Isophenolphthalein	....	3400	4115
Benzaurin	2900	3380	4050

Table I gives the frequency numbers of the peaks of the bands in the various solutions of phenolphthalein, isophenolphthalein and diphenylphthalide.

TABLE I

FREQUENCY NUMBERS OF BANDS

Solvent	*Diphenyl-phthalide*	*Phenol-phthalein*	*Isophenol-phthalein*
Neutral absolute alcohol	3531	3523	3511
	3620	3613	3606
	3711		
	3769		
	3861		
	3960		
Concd. sulfuric acid		2025	2000
	2243		2225
	2450	2560	2350
		3085	
	3277	3555	3500
	3946	3875	3850
Alcoholic KOH—23 molecules		1785	1695
		2730	2525
			2855
		3523	3525
		3625	3615
Alcoholic KOH (Phenolphthalein—232 molecules) (Isophenolphthalein—171 molecules)		1785	1695
		2730	2440
		3400	3400
		3950	4060
33% aqueous KOH		3380	3400
		4065	4115

We are much indebted to Mr. C. V. Shapiro[13] for his assistance in the preparation of our data for publication.

Summary

1. The absorption curves of phenolphthalein, isophenolphthalein and of diphenylphthalide (the mother substance of the two phthaleins) in neutral absolute alcohol have been determined and their relation pointed out.

2. The absorption curves for the three above-mentioned substances in concd. sulfuric acid solution have been determined and their resemblances and differences indicated.

3. The effect of the addition of various amounts of potassium hydroxide to the alcoholic solutions of phenolphthalein and isophenolphthalein due to the formation of the potassium salts has been studied. It has been suggested that the salts of isophenolphthalein have an *o*-quinoid structure while those of phenolphthalein are *p*-quinoid.

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[13] Heckscher Research Assistant in Physics and Chemistry, Cornell University, 1923–26.

4. The absorption curves for the colorless solutions of phenolphthalein and isophenolphthalein in 33% aqueous potassium hydroxide have been determined. The absorption is due to the presence of the colorless tripotassium salt of the carbinol-carboxylic acid.

5. A table showing the frequency numbers of the peaks of the bands of the various solutions studied has been prepared.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE POLARIMETRY SECTION OF THE BUREAU OF STANDARDS, UNITED STATES DEPARTMENT OF COMMERCE][1]

RELATIONS BETWEEN ROTATORY POWER AND STRUCTURE IN THE SUGAR GROUP. XVI.[2] CONVERSION OF CELLOBIOSE TO ANOTHER DISACCHARIDE, CELTROBIOSE, BY THE ALUMINUM CHLORIDE REACTION. CHLORO-ACETYL CELTROBIOSE

BY C. S. HUDSON

RECEIVED MAY 22, 1926 PUBLISHED JULY 6, 1926

The new method of chlorinating sugar acetates by aluminum chloride which Kunz and the writer have described in the preceding article has been applied to cellobiose octa-acetate with the result that a considerable yield of the well-known crystalline α-chloro-acetyl cellobiose has been obtained, and in addition a yield of about 13% of an isomeric crystalline substance, the properties of which show that it is the chloro-acetyl derivative of a new disaccharide. It has been carefully purified by repeated crystallizations until its rotation became constant at $[\alpha]_D^{20} = +59.2$ in chloroform solution. The melting point was 137–138°. Its chlorine content was found to be 5.43% by heating it in acetic anhydride solution with silver acetate and 5.40% by Bacon's directions[3] for the Stepanoff method. The theoretical value for a chloro-hepta-acetyl dihexose, $C_{26}H_{35}O_{17}Cl$, is 5.41%. Its saponification by potassium hydroxide at 0° according to Kunz' method (see preceding article) shows its acid equivalent to correspond closely with that calculated. The alkaline saponification of the new chloro-acetate yields a dextrorotatory solution from the reading of which it is evident that the parent sugar is weakly dextrorotatory. After hydrolysis of the new chloro-acetate with 0.5 *N* hydrochloric acid for two and a half hours at 98°, by which treatment it is to be expected that the chlorine and acetyl groups are split off and the parent disaccharide largely hydrolyzed to its component hexoses, the solution is strongly levorotatory. These analytical, melting-point, rotation and hydrolysis data differentiate the sugar from all

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[1] Published by permission of the Director of the Bureau of Standards.

[2] See preceding Article XV.

[3] Bacon, THIS JOURNAL, 31, 49 (1909).

known disaccharides and it is accordingly a new di-hexose and will be named *celtrobiose*. The crystalline derivative of it which results from the action of aluminum chloride upon the chloroform solution of cellobiose octa-acetate is accordingly named *chloro-acetyl celtrobiose*. Since the aluminum chloride reaction chlorinates the octa-acetates of both lactose and cellobiose and also partially changes them to chloro-acetyl derivatives of new sugars, it appears that the reaction is a general one for the chlorination of sugar acetates and possibly also for intramolecular rearrangement. In conformity with this view it has been found that α-chloro-acetyl glucose ($[\alpha]_D = +166$ in chloroform; m. p., 74°) is produced from β-glucose penta-acetate in considerable quantity by the reaction; whether some other chloro-acetate of a hexose is produced as a by-product in this case remains to be investigated. Studies of the application of the reaction to various sugar acetates and likewise an investigation of the possibility of preparing in analogous manner bromo- and iodo-acetyl sugar derivatives by the use of aluminum bromide or iodide are in progress at this Bureau.

Preparation of Chloro-acetyl Celtrobiose ($C_{26}H_{35}O_{17}Cl$).—Ten g. of recrystallized cellobiose octa-acetate ($[\alpha]_D = +36$ in chloroform; m. p., 221°) was dissolved in 100 cc. of absolute chloroform, 40 g. of powdered active aluminum chloride was added and the mixture was gently refluxed for five hours, using a calcium chloride tube to keep out moisture. It was then poured upon cracked ice, the mixture was well shaken and the chloroform layer was washed twice with ice water, dried with calcium chloride and evaporated under reduced pressure to small volume. The addition of ether caused an immediate voluminous precipitation of needle-like crystals which were filtered off and recrystallized by dissolving in a little chloroform and adding ether. The weight was 3.5 g.; $[\alpha]_D^{20} = +58.2$ in chloroform. The crystals are a mixture of substances which are difficult to separate, but by fractional crystallization from alcohol one component ($[\alpha]_D^{20} = +70$ in chloroform; m. p., 184°) was obtained fairly pure and the data indicate that it is the well-known α-chloro-acetyl cellobiose ($[\alpha]_D = +73$; m. p., 187°).[4] The original mother liquor was concentrated under reduced pressure to small volume, taken up with ether and filtered from a new crop of needle crystals. The filtrate soon deposited on the beaker walls a new type of crystal, hexagonal plates, with which needles could also be seen. By fractional crystallization from ether the two substances were separated and 1.3 g. of hexagonal plates, free from needles, was obtained. They were dried at 35° in air, then in a desiccator over lime and it was found that heating them at 100° caused no further loss in weight. The substance is a chloro-hepta-acetate of a new disaccharide (di-hexose), celtrobiose. After several recrystallizations from chloroform or ether by the addition of petroleum ether the rotation of the chloro-acetate became constant at the

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[4] Schliemann, *Ann.*, **378**, 374 (1911).

value $[\alpha]_D^{20} = +59.2$ in pure chloroform (1.0878 g. of substance, 25 cc. of chloroform solution; 5.154° rotation to the right in a 200mm. tube). The substance melted at 137–138° without decomposition but slowly decomposed with gas evolution in the range 155–165°. A chlorine estimation was made by heating 1.056 g. of substance with 0.4 g. of pure silver acetate in acetic anhydride solution for one hour on the steam-bath and weighing the silver chloride (0.2269 g.); 5.43% of chlorine was found as compared with 5.41% calculated for $C_{26}H_{35}O_{17}Cl$. A measurement by Bacon's directions for the Stepanoff method showed 5.40% of chlorine (0.1938 g. of substance gave 0.0414 g. of silver chloride), which proves that the substance contains only one chlorine atom in its molecule. The ease of removal of this atom by silver acetate corresponds with the behavior of chloro-acetyl derivatives of the sugars. The acid equivalent was found by saponifying in an ice-salt bath 0.2011 g. of substance dissolved in 50 cc. of acetone with 50 cc. of 0.1 *N* potassium hydroxide aqueous solution for two hours; the alkali that was neutralized was 24.4 cc. as compared with the calculated value 24.5 cc. Chloro-acetyl celtrobiose is very soluble in chloroform or acetone, somewhat soluble in warm ether, nearly insoluble in cold ether, insoluble in petroleum ether or water. It reduces Fehling's solution on boiling. It is a stable halogeno-acetyl sugar derivative and may be kept in moist air without decomposition.

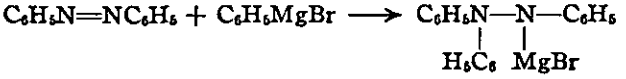
Summary

The action of active aluminum chloride on a chloroform solution of cellobiose octa-acetate produces the well-known α-chloro-acetyl cellobiose and in addition an isomeric substance that proves to be the chloro-hepta-acetate of a new di-hexose to which the name celtrobiose is given.

WASHINGTON, D. C.

NOTE

The Mechanism of Reduction of Azobenzene by Organomagnesium Halides.—Several theories have been proposed for the mechanism of reduction of azobenzene by organomagnesium halides. Busch and Hobein[1] suggested tentatively that phenylmagnesium bromide added to azobenzene as follows.



$$C_6H_5N{=}NC_6H_5 + C_6H_5MgBr \longrightarrow \underset{H_5C_6}{C_6H_5N}{-}\underset{MgBr}{N}{-}C_6H_5 \qquad (I)$$

This was proposed as a possible explanation for the formation of triphenylhydrazine from β-phenylhydroxylamine and phenylmagnesium bromide. Franzen and Deibel[2] interpreted the formation of hydrazobenzene as follows.

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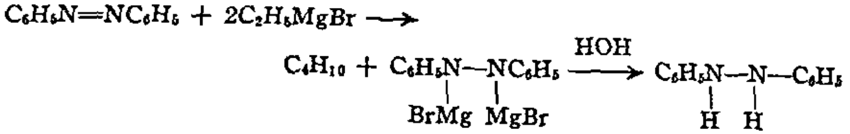
[1] Busch and Hobein, *Ber.*, **40**, 2099 (1907).

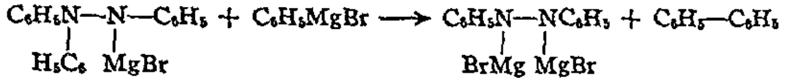
[2] Franzen and Deibel, *Ber.*, **38**, 2716 (1905).



$$C_6H_5N{=}NC_6H_5 + 2C_2H_5MgBr \longrightarrow C_4H_{10} + \underset{BrMg}{C_6H_5N}-\underset{MgBr}{NC_6H_5} \xrightarrow{HOH} \underset{H}{C_6H_5N}-\underset{H}{N}-C_6H_5 \qquad (II)$$

Gilman and Pickens[3] showed that the latter mechanism (II) is correct. This was done by replacing the —MgBr groups of the intermediate compound by groups that give known hydrazobenzene derivatives. For example, when the reaction product of azobenzene and an RMgX compound is treated with benzoyl chloride prior to hydrolysis, a good yield of dibenzoyl-hydrazobenzene is obtained, in addition to a corresponding amount of the expected R–R compound.

However, it is possible for both mechanisms (I and II) to be correct. In each experiment[3] a slight excess over two molecular equivalents of Grignard reagent was used with one equivalent of azo compound. Reactions I might first have taken place. Then the second equivalent of RMgX compound may have reacted as follows.



$$\underset{H_5C_6}{C_6H_5N}-\underset{MgBr}{N}-C_6H_5 + C_6H_5MgBr \longrightarrow \underset{BrMg}{C_6H_5N}-\underset{MgBr}{NC_6H_5} + C_6H_5-C_6H_5 \qquad (III)$$

Experiment has shown that the mechanism postulated in (III) is incorrect. When triphenylhydrazine was treated with an excess of phenylmagnesium or ethylmagnesium bromide, under conditions that convert azobenzene to hydrazobenzene, no reaction occurs and practically all of the triphenylhydrazine is recovered. Accordingly Reaction I does not precede Reaction II.[4]

Triphenylhydrazine and Ethylmagnesium Bromide.—An ether solution of 5 g. (0.019 mole) of triphenylhydrazine and 0.1 mole of ethylmagnesium bromide was refluxed for eight hours, allowed to stand overnight, and then hydrolyzed by an ammoniacal ammonium chloride solution. The ether layer, when worked up in the customary manner, gave 4.6 g. of triphenylhydrazine.

Triphenylhydrazine and Phenylmagnesium Bromide.—Five g. (0.019 mole) of triphenylhydrazine was treated with 0.058 mole of phenylmagnesium bromide under the conditions described for ethylmagnesium bromide. Four g. of pure triphenylhydrazine was directly recovered as well as 0.3 g. of impure triphenylhydrazine from the mother liquors.

CONTRIBUTION FROM THE CHEMICAL
LABORATORY OF IOWA STATE COLLEGE
AMES, IOWA

HENRY GILMAN
CHESTER E ADAMS

RECEIVED APRIL 28, 1926
PUBLISHED JULY 6, 1926

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[3] Gilman and Pickens, THIS JOURNAL, 47, 2406 (1925).

[4] It has already been stated (Ref. 3, p. 2415) that diazonium salts do not show the reaction of RN=NR compounds towards the Grignard reagent. However, diazosulfones appear to undergo the same type of reaction as azo compounds towards organomagnesium halides.

The *sym.*-diphenyl-tribenzoyl-triazane $[(C_6H_5)(C_6H_5CO)NN(COC_6H_5)N(COC_6H_5)(C_6H_5)]$ obtained from diazo-aminobenzene, ethylmagnesium bromide and benzoyl chloride and described on p. 2411 of Ref. 3 has been analyzed by J. E. Kirby. Calcd. for $C_{33}H_{25}O_3N_3$: N, 8.22. Found: 8.37.

NEW BOOKS

Handbuch der Physik. Edited by H. GEIGER AND KARL SCHEEL. Volume X. Thermische Eigenschaften der Stoffe, edited by F. HENNING. Julius Springer, Linkstr. 23–24, Berlin W 9, 1926. vii + 486 pp. 207 figs. 26 × 17.5 cm. Price Reichsmark 35.40, unbound; Reichsmark 37.50, bound.

This "Handbuch," by a large number of authors (German, with very few exceptions) is appearing in 24 volumes, of which Vols. 1–8 deal with the fundamentals of physics, Vols. 9–11 with heat, Vols. 12–17 with electricity and magnetism, Vols. 18–21 with optics of all wave lengths, and Vols. 22–24 with the structure of matter and the nature of radiation. This tenth volume is made up of eight chapters as follows: Solids (pp. 1–59) by E. Grüneisen; Fusion, Crystallization and Sublimation (pp. 60–125) by F. Körber; Gases and Liquids (pp. 126–222) by J. D. van der Waals, Jr.; Thermodynamics of Mixtures (pp. 223–274) by P. Kohnstamm; Specific Heat, theory (pp. 275–320) by E. Schrödinger; Specific Heat, experimental (pp. 321–349) by K. Scheel; The Determination of Free Energy (pp. 350–404) by F. Simon; Thermodynamics of Solutions (pp. 405–480) by C. Drucker. The book is a characteristic German compilation; as usual the treatment is theoretical and exhaustive but unimaginative and hardly suggestive of new inquiries; and it does not always distinguish sufficiently between formulas based on theory and formulas which involve some approximation or assumption. The mode of presentation would offer some difficulties to an American reader unacquainted with the topic, and might cause him some misapprehension as to the way in which the topic developed historically; for, on a rough estimate, ninety per cent. of the references are to German books and authors of recent date, and most of the remaining ten per cent. are to Hollanders. Indeed, in as far at least as this volume is concerned, the title might almost be "Handbuch der deutschen Physik."

J. J.

L'Énergétique des Réactions Chimiques. (The Energetics of Chemical Reactions.) By Professor G. URBAIN, Paris. Librairie Octave Doin, 8, Place de l'Odéon, Paris, 1925. viii + 267 pp. 102 figs. 21.5 × 13.5 cm. Price 27 fr.

The object of this book is to provide, in a French text, a rigorous treatment of the fundamental propositions of thermodynamics, in a form adapted to the needs of the chemist, as distinguished from the physicist or mathematician. The author strives to eliminate from his work all analogies from mechanical theory and considerations of mathematical elegance, and to proceed always by steps which can be objectively visualized. The use of such abstract functions as entropy and thermodynamic potential is minimized. Considering that the greatest triumphs of modern science are being won precisely by the relentless pursuit of abstractions, regardless of the possibility of objective visualization, the reviewer is not greatly in sympathy with M. Urbain's aim.

The method of introducing and defining the primary concepts is unusual and interesting. Quantity of heat is first defined as proportional to the mass of a standard substance which melts or solidifies at constant temperature, when the process under discussion is conducted so as to leave no changes in any other body than the calorimetric substance. Temperature receives at once the thermodynamic definition in terms of the efficiency of the Carnot cycle. A perfect gas is defined as a substance of which the energy is independent of the volume and the volume inversely proportional to the pressure at constant temperature. The thermal expansion of such a substance must be proportional to the thermodynamic temperature scale. Several propositions concerning isotherms and adiabatics are demonstrated.

Much emphasis is placed on the distinction between thermal and elastic changes and chemical changes. A system in which the former occur freely, but the latter are inhibited, is said to be in chemical constraint. The operator is supposed to possess suitable catalysts, by means of which he can control the velocity, but not the direction, of all changes.

The material of the rest of the book follows conventional lines. Homogeneous gas systems receive the largest share of quantitative treatment. Solutions are considered only in so far as their osmotic pressure obeys the gas law. Heterogeneous systems are described from the standpoint of the phase rule. The ten pages devoted to the third law are essentially a condensation of the corresponding chapter in Nernst's *Theoretical Chemistry*, and contain no reference to American work in this field.

However well this book may meet the special purpose for which it was written, it can hardly be considered as a significant addition to the world's literature of chemical thermodynamics.

ALBERT SPRAGUE COOLIDGE

Quantitative Analysis. By JAMES M. HENDEL, Ph.D., Assistant Professor of Chemistry, Hunter College of the City of New York. Ginn and Company, 15 Ashburton Place, Boston 2, Massachusetts, 1925. vi + 138 pp. 8 figs. 19 × 13 cm. Price $1.40.

This book is intended to serve as the basis for one year's work in quantitative analysis. Any criticism must be directed mainly toward errors of omission rather than toward those of commission, for the little book is quite good as far as it goes. It is plain, however, that students using this text would be dependent upon class-room instruction for much information which might well be given in an instruction book in quantitative analysis.

The contents are divided into the conventional groups of gravimetric, volumetric, electrometric and electrolytic methods. The material given in the first two groups is not quite generous enough to enable students to pass examinations given in many universities on the basis of one year's work. Whether this lack is compensated by the devotion of considerable space to the subject of electrometric titrations is an open question. To the reviewer it seems wiser to lay the foundations more firmly, and to reserve electrometric methods for a later course.

The book is well put together, in the main well written, and if accompanied by well planned class-room work, it should prove quite satisfactory for a short course.

PAUL H. M.-P. BRINTON

Gmelins Handbuch der anorganischen Chemie. (Gmelin's Handbook of Inorganic Chemistry.) Edited by R. J. MEYER. Eighth edition. The Noble Gases: Helium, Neon, Argon, Krypton, Xenon and Emanation. System No. 1. Published by the Deutsche Chemische Gesellschaft, Verlag Chemie, G.m.b.H., Leipzig-Berlin, Germany, 1926. xxxii + ix + 251 pp. 6 figs. 25.5 × 17.5 cm. Price, singly, M. 39; to subscribers to the entire work, M. 29.50; postage extra.

This volume, the third instalment to appear, is really Volume I of this excellent encyclopedia of inorganic chemistry. In addition to its specific subject matter, it contains a general introductory section, comprising a preface to the entire work, a statement as to the method of presentation, directions for the use of the handbook and a list of the journals referred to and their abbreviated titles.

In the preface, the Editor-in-Chief, R. J. Meyer, describes in greater detail than in previous notices the guiding principles which have determined the scope and nature of this encyclopedic handbook. He reiterates that the whole undertaking will be completed in ten years (1935) and states that in general the order of appearance of the separate parts will be determined by two main considerations, namely, the period which has elapsed since the corresponding volume of the former (seventh) edition appeared and the importance of the element.

As regards the method of presentation, it is of interest that the use of the suffixes o and i and ul and ür has been abandoned and the valence number in Roman type substituted; thus, instead of ferrisulfat and eisenchlorür are written eisen^{III}sulfat and eisen^{II}chlorid.

Furthermore, in spite of æsthetic considerations, whenever feasible and exact, the formulas have been substituted for the names of chemical substances. This has unquestionably led to a great saving of space, and doubtless also has actually increased the speed of reading. It is, however, amusing to find this urge toward brevity becoming so pronounced that the editor, a German, protests strongly against the *long polysyllabic* names used by Mellor in his Treatise on Inorganic and Theoretical Chemistry!..

In the remainder of the volume dealing with the noble gases, there is an introduction telling of the discovery and occurrence of these gases; thereafter, each gas is described separately. The subject matter is of course largely physics rather than chemistry, but the authors have wisely decided to present it fully nevertheless. The literature up to July, 1925, has been covered.

The volume is unique, and will be indispensable in every laboratory and library at all concerned with the noble gases.

The editors collaborating in this volume were Friedrich Struwe, Reinhold Johow and Erich Pietsch.

Arthur B. Lamb

General Chemistry: An Elementary Survey Emphasizing Industrial Applications of Fundamental Principles. By Horace G. Deming, Professor of Chemistry, University of Nebraska. Second edition, thoroughly revised. John Wiley and Sons, Inc., New York; Chapman and Hall, Limited, London; 1925. xvi + 650 pp. 128 figs. 22 × 14 cm. Price $3.50.

The introductory chapters of this book, which attained a marked success upon its first appearance about two years ago, have been entirely rewritten. Generalizations, even including a discussion of the structure of the atom, which were formerly scattered in the later chapters, have been gathered together and placed at the beginning. Thus the chapter on oxygen, which began on p. 17 of the first edition, begins on p. 55 in this edition. Teachers who believe that fundamental definitions, laws, and the use of formulas should be presented before any of the systematic consideration of the properties of the elements and their compounds will undoubtedly consider the change an improvement. Teachers, however, who contend that generalizations require some previous knowledge of descriptive chemistry for a foundation will probably not favor the new arrangement. The basis of this criticism is very much weakened by the very successful way in which the author makes use of common things and familiar phenomena to illustrate principles and of clever analogies to clarify more difficult generalizations.

The chapter on organic compounds has been entirely rewritten and somewhat shortened. Otherwise, the descriptive parts of the book are little changed and it retains that characteristic which the author himself stated in the preface of the first edition as follows: "It is hoped that this book may be appreciated for the things it has left unsaid. Most texts contain too much matter that properly belongs in a course of descriptive inorganic chemistry for students specializing in chemistry." By sacrificing what is termed "museum material," space is gained for topics of more lively interest and for a style of presentation more readable, if less concise, than that of many popular texts.

Kenneth L. Mark

Trattato di Chimica Generale ed Applicata all' Industria. Vol. I. Chimica Inorganica. Parte Seconda. (Treatise on General Chemistry in its Application to the Industries. Vol. I. Inorganic Chemistry. Second Part.) Fifth edition revised and enlarged. By Dr. ETTORE MOLINARI, Professor of Chemical Technology, Milan. Ulrico Hoepli, Milan, 1925. viii + 671 pp. 164 figs. 24 × 16.5 cm. Price L. 45.

This "Part" of Vol. 1, paged from 681 to 1351, covers the elements and their compounds, in the scheme of classification followed, from arsenic to boron, of the non-metals, and then all of the metals. Some idea of the extent to which this book is grown may be obtained by a comparison of this "part" with Feilmann's English translation of the third Italian edition of the volume on "Inorganic Chemistry," in which the treatment of the above-mentioned topics covers 244 pages. Thus, there is an increase of 388 pages in this last edition, but also there is a large increase in the use of lower case type; hence, the increase in matter is really greater than the increase in pages alone would indicate. The evidences of revision are everywhere to be observed and the pure as well as the applied and statistical features have benefited. It is amazing how many-sided this presentation of chemistry is and this fact no doubt has, in a large measure, contributed to the wide acceptance this publication has met. It has been much used as a textbook in former editions, but it is becoming now so encyclopedic as to be likely to be used only as a work of reference. It will be found especially valuable for such use because of its wide range of topics, its many points of view, and its evidence of earnest and capable efforts to keep the record up to date.

CHARLES E. MUNROE

Untersuchung und Nachweis organischer Farbstoffe auf spektroskopischem Wege. By Professor Dr. J. FORMÁNEK, in Prag and Professor Dr. J. KNOP, in Brünn. Second revised and enlarged edition. Part second, third instalment. Julius Springer, Berlin, 1926. 208 pp. 41 figs. 12 plates. 24.5 × 16.5 cm. Price, unbound, Reichsmark 36.

The present instalment, the third in this part, deals with yellow dyes, including numerous orange and brown dyes, under three divisions. In the first division, dyes with bands which may be located exactly or with fair accuracy in the usual solvents by visual methods are tabulated in nine main groups and five additional sub-groups. The tables include 231 color types. In the second division are listed 173 color types of yellow dyes which afford visual identification only in solution in concentrated sulfuric acid. The third division, including 60 color types, comprises yellow and brown dyes of which the bands lie principally in the ultraviolet, necessitating the resort to photographic methods of measurement. The index lists 1365 technical brands which were investigated.

Formánek and Knop's methods are spectroscopic rather than spectrophotometric. The general constitutional groups of dyes are recognized by the general form of their spectra and the type of their modification under suitable modifications of concentration and solvents, and dependence is placed upon precise determinations of the locations of absorption maxima for the identification of individual dyes within these groups. The methods have their limitations. "Dyes tabulated together are not necessarily chemically identical. Band spectra are less accurately located than line spectra, especially near the limits of the visual spectrum. Qualitative spectroscopic identity indicates close constitutional relationship, however, if not complete identity." It may be admitted, however, that their spectroscopic scheme affords a very convenient means of identifying a large number of yellow dyes with as great precision as is ordinarily desired. For a further differentiation between dyes of closely related constitution the determination of suitable spectrophotometric constants (ratios) will doubtless frequently prove effective.

A wealth of spectroscopic data is presented in a field in which previous investigations have been relatively limited and the volume will be indispensable to the dye spectroscopist. An excellent treatment of photographic equipment and technique for the ultraviolet is included.

The long delay in the publication of this third instalment is attributed to the war, to the severe illness of the senior author and to the necessity of investigating photographic as well as visual methods. The fourth instalment, which will deal primarily with vat dyes and lake colors, is promised at an early date.

W. C. Holmes

Physiological and Clinical Chemistry. By William A. Pearson, M.D., Professor of Physiological Chemistry and Joseph S. Hepburn, Ph.D., Associate Professor of Chemistry, in the Hahnemann Medical College of Philadelphia. Lea and Febiger, Philadelphia and New York, 1925. xvi + 306 pp. 30 figs. 20.5 × 14 cm. Price, $4.00.

This book is essentially a laboratory manual. It differs from most laboratory manuals in that it includes a considerable amount of text such as is ordinarily found only in textbooks of physiological or clinical chemistry. The subject matter is astonishingly complete; practically all the common tests and methods are presented. While this is a convenience to the mature worker, it must be confusing to a student and to the average clinician who is capable of exercising little critique in evaluating the relative dependability and accuracy of a test or method. While the book contains the great bulk of the quantitative methods that are in common use, their presentation is not very critical and the book is essentially qualitative rather than quantitative. It is a good representative of the type of book which is useful in the kind of qualitative teaching of biochemistry that is rapidly disappearing. The teaching of biochemistry is becoming quantitative. The point of view of the most progressive teachers is not that of this book. Modern teaching of biochemistry should be not merely quantitative but must be based primarily on the point of view of physical and colloidal chemistry. This book is almost devoid of any treatment of the subject matter from the point of view of these two important branches of modern chemistry. For example, in considering enzymes there is no discussion of equilibria or of the well-known laws of catalysis. There is no discussion of the colloid state. The whole matter of hydrogen-ion concentration is relegated to the Appendix. Methods for its determination are given without any indication of their significance.

The book is a useful one for those who are giving the type of qualitative descriptive course for which it is designed. It is useful to mature workers as presenting in convenient form a nearly complete collection of tests and methods. For such workers, however, its value is impaired by reason of the complete absence of references to the literature. It is not suitable for modern courses which stress the dynamics of living matter, quantitative measurements, and the point of view of physical and colloidal chemists.

CARL L. ALSBERG

Methoden zur Bestimmung der Zusammensetzung der Nahrungsmittel der Pflanzen. (Methods for the Determination of the Composition of Plant-foods.) By H. NEUBAUER. Urban and Schwarzenberg. Friedrichstrasse 105b, Berlin N 24, Germany, 1925. 145 pp. 3 figs. 25.5 × 18 cm. Price, unbound, M. 6.

This book constitutes an integral part of volume XI of Abderhalden's monumental work, "Handbuch der biologischen Arbeitsmethoden." In consequence, its pages run from 467 to 612 and it lacks both a table of contents and an index since these appear only in the final number of each volume. It would have been far more appropriate to have used the supplementary title, "Analyse der Düngemittel," as the name of this publication since its contents are confined almost exclusively to the methods that are employed to determine nitrogen, phosphoric acid, potash and lime in fertilizers. Section one contains such general observations and directions for the execution of analyses as generally appear in works devoted to analytical procedure; section two gives detailed descriptions of the more important methods employed in fertilizer analysis, the determinations of nitrogen in its several forms, phosphoric acid, potash, soda, lime and magnesia being taken up in turn; while section three contains special directions for the examination of commercial fertilizers and particular agricultural materials used as fertilizers. Though the American chemist usually confines himself to the prescribed methods contained in "Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists" yet there is much in Neubauer's work that will prove of value to referees of that Association in their endeavors to perfect those methods, as well as to those interested in the study of the relative accuracy of different analytical procedures. References are numerous but restricted, with three exceptions, to German articles.

Cochineal, commonly used in this country as an indicator for nitrogen determinations, is not mentioned. Ammonium chloride and sulfate, prepared from synthetic ammonia, are suggested as convenient and reliable substances for standardization in alkalimetric work. The former of these has, in fact, been adopted by the Verein Deutscher Dünger-Fabrikanten in their "Methoden zur Untersuchung der Kunstdüngemittel," Braunschweig, 1925. The Jodlbauer and Förster modification of the Kjeldahl method (involving the use of salicylic acid and sodium thiosulfate) is considered obsolete and displaced by methods (those of Ulsch, Devarda and Arnd) involving reduction by nascent hydrogen. The Arnd method is especially recommended as likely to displace the use of Devarda alloy, and its use in combination with the Kjeldahl procedure is stated to be simpler and more accurate than our official modified Kjeldahl (and Gunning) method for the determination of total nitrogen where nitrate nitrogen is present.

It appears to the reviewer that too much stress is laid on the Lorenz molybdate method for phosphoric acid, the composition of the dry molybdate precipitate being admittedly uncertain. The use of the Lorenz method in physiological investigation where comparatively small quantities of phosphoric acid are to be determined is, no doubt, highly desirable and sufficiently accurate but it cannot and does not meet the needs of the fertilizer chemist. The discussion of the molybdate method with subsequent determination of the phosphoric acid as magnesium pyrophosphate is unusually thorough and good, doubtless due to Neubauer's extensive study of this procedure. His conclusions and results closely check those of Lundell and Hoffman (J. Assoc. Official Agr. Chemists, Vol. 8, No. 2).

The determination of potash as potassium platinic chloride, while official for this country and used by the Verein Deutscher Dünger-Fabrikanten, is merely mentioned and several pages are devoted to the Finkener-Neubauer method whereby the potassium platinic chloride is reduced by illuminating gas and weighed as metallic platinum.

The final section is especially valuable to the chemist confronted with such problems as the determination of perchlorate and chlorate in nitrates, of cyanamide, dicyanamide and calcium carbide in Cyanamid, and so forth.

Albert R. Merz

Gesammelte Abhandlungen zur Kenntnis der Kohle. (Collected papers on Knowledge of Coal.) Edited by *Professor* Dr. Franz Fischer, Director of the Kaiser-Wilhelm Institute for Coal Research in Mülheim-Ruhr. Seventh volume (for the years 1922–1923). Gebrüder Borntraeger, Berlin, 1925. viii + 308 pp. 25.5 × 16.5 cm. Price, unbound, Gm. 16.50.

This volume contains 43 papers (of which 33 are previously unpublished) and an appendix of brief abstracts of 43 papers published in *Brennstoff*

Chemie. The work of the Kaiser-Wilhelm Institute for Coal Research for the years 1922 and 1923 is reported in these papers.

The subject matter may be grouped as follows: I, Synthesis, starting with carbon monoxide; II, Oxidation of methane; III, Reduction of phenols to benzene; IV, Investigations on primary (low temperature) tar; V, Properties of various kinds of coke; VI, The lignin origin of coal; VII, Electrochemical researches; VIII, Analytical methods; IX, Lectures.

One-third of the volume is devoted to reviews of the literature and giving results of experiments on the catalytic decomposition of carbon monoxide, formaldehyde, methyl alcohol, formic acid, and "Synthol" at various temperatures and in the presence of various metals, metal oxides and carbonates. Chemists interested in syntheses from carbon monoxide and hydrogen will find much empirical information on the effect of contact substances, principally metals, metal oxides and carbonates, on these reactions, and on the reduction of carbon monoxide to formaldehyde and to methanol, at atmospheric pressure. No attempt is made to develop any systematic theoretical treatment of these catalytic reactions from a physicochemical point of view.

Coal chemists will be interested in the group of papers on primary tar, coke, and the origin and constitution of coal, which comprise another third of the book.

The third important group of papers deals with electrolytic investigations on the production of formic acid, the cathodic behavior of carbon in aqueous solutions, the anodic oxidation of formic acid, the electrochemical utilization of solid and liquid fuels, etc. In studying the cathodic behavior of carbon in aqueous solutions, the principal objective was the reduction of carbon at the cathode to methane by the evolved hydrogen. Although the results were negative, the authors are to be commended for publishing this research as well as a number of other researches which likewise led to negative results.

The work of Fischer and his associates should not be judged from the collected papers of this volume but rather by the collected references in the appendix to papers published during this period in *Brennstoff Chemie,* the major researches being published in that journal. The previously unpublished papers which comprise this volume are largely reviews of the literature, minor researches and the various odds and ends that complete the record of the years 1922 and 1923.

A. C. Fieldner

AMERICAN CHEMICAL SOCIETY

FIFTY-FIRST YEAR

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ACTIVITY COEFFICIENTS OF TERVALENT IONS IN VERY DILUTE SOLUTIONS

By J. N. Brönsted and N. J. Brumbaugh

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Introduction

In the study of activity coefficients, the method of measuring solubilities combines great simplicity with a high degree of accuracy even in the region of great dilution. As these very dilute solutions present interesting theoretical considerations, it seemed important to extend previous work on this problem[1] to salts of still less solubility. In such an investigation it is expedient for experimental reasons to use saturating salts of a high valence type, as otherwise the change in solubility in dilute-solvent solutions would scarcely suffice for exact determinations.

The present investigation covers determinations of the solubility of the tervalent salt *luteocobaltic-hexacyano-cobaltiate:* $Co(NH_3)_6Co(CN)_6$ in sodium chloride solutions ranging from 0 to 0.02 molal. The solubility of this salt is comparable in magnitude to that of silver chloride. Notwithstanding this fact it has been possible, on account of its sensitiveness towards changes in concentration of the salt solution serving as solvent, to fix the solubility curve with an accuracy quite sufficient for our purpose, that is, to determine whether the data obtained in this investigation will lead to the same equations as the data obtained in the previous investigation.[1] The same salt has served in a previous investigation[2] to illustrate the enormous increase in solubility shown by salts of this high valence type upon addition of other electrolytes. The concentration of the added salt in the previous investigation, however, was not less than 0.05 *N*.

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[1] Brönsted and La Mer, This Journal, 46, 555 (1924).

[2] Brönsted and Petersen, *ibid.*, 43, 2265 (1921).

Experimental Part

The apparatus and methods for obtaining saturated solutions were the same as those designed by Brönsted and La Mer for the investigation to which reference has already been made. The four solubility cells shown in the figure of that paper were charged with the luteo salt in a fine crystalline state forming a column of 10 to 12 cm. in height. The solvent solutions were continuously flowing through the salt columns with a speed of about 1.5 liters per 24 hours. In two of the cells the flow was not interrupted for a period of more than four months, about 200 liters of water or sodium chloride solution running through in that time. The amount of solid salt dissolved during this period, however, did not exceed 2 g. It was thus not necessary to renew the charge of solid salt in the cells.

Because of the very slight solubility of the luteo salt, it was necessary to use a volume of at least 1000 cc. of the saturated solution for each analysis. After adding 1 cc. of N sulfuric acid, about 900 cc. of water was evaporated from this volume by distillation from a 2-liter flask. After cooling, 5 cc. of a 10% solution of potassium hydroxide was added to the remaining 100 cc. The flask was then directly connected to a quartz condenser and about 50 cc. of the solution distilled. This 50 cc. of distillate which, as it was determined, contained all the ammonia, was collected in a very slight excess of 0.02 N sulfuric acid. After a current of pure air had been passed through the distillate for not less than 15 minutes in order to remove carbon dioxide, which might have been present in traces, the titration was made with the air current continuing.

The indicator used for the titration was bromocresol purple with a color standard of the same substance in the presence of a citrate buffer whose Sörensen (P_{H}) value was 6.0. This Sörensen value is the correct one for the titration of very dilute ammonia solutions.

Under the conditions described above, the color change caused by 0.01 cc. of the 0.02 N acid or base is easily detectable with this excellent indicator. Nevertheless, separate experiments with identical solutions could not be made to coincide with this degree of accuracy. During the several operations necessarily involved in each analysis, experimental errors accumulated amounting in some cases to 0.1 cc. of a 0.02 N solution and in a few analyses to even more. By taking the average of a great number of single experiments, however, it is evident that errors originating in such accidental deviations will be very largely eliminated. It is, therefore, reasonable to conclude that the average values of the data have an accuracy sufficient for the purpose of this paper as stated above.

As emphasized in the article already referred to, the advantage of the above method for determining solubilities consists particularly in the fact that saturation is reached by bringing the various solvents into contact with the same unchanging sample of the solid salt. A test of the reliability of a determination can be made by using pure water or another solvent at the beginning of the experiment and the same solvent after the series of determinations have been finished. Agreement between the initial and final values would prove the saturating salt to have remained unchanged.

The Data Obtained

The measurements were carried out by first running water through the cells for from one to two weeks (initial period). Then the solvent was changed to the sodium chloride solutions of various molalities (salt period). Finally, pure water was again used as the solvent in order to check the values found for water as solvent at the beginning of the series of determinations (final period).

Table I gives the data for the solubility of the luteo salt in water. The values given in Table I are the cubic centimeters of 0.01793 *N* sulfuric acid used for the neutralization of the ammonia present in 1 liter of the saturated solution of the luteo salt. From the average of the three final values of each series, that is, from 4.58 cc., 4.60 cc. and 4.61 cc. of acid used for neutralization was calculated the solubility of the luteo salt in water at 18°. This was found to be 1.375×10^{-5} of a mole of the luteo salt. The column of averages indicates that there was little change in the salt at the beginning and at the end of the run. The above value, 1.375×10^{-5} *M* of luteo salt is used in Table II as the 0 molal value for sodium chloride.

The total number of analyses made for the solubility of the luteo salt in pure water was 77.

TABLE I

SOLUBILITY OF LUTEOCOBALTIC-HEXACYANO-COBALTIATE IN WATER AT 18°

FIRST SERIES

		Cell 1	Cell 3	Av.
Initial period	No. of detns.	11	13	
	Mean value of single detns.	4.56	4.63	4.60
Salt period	NaCl solns. of 0.001, 0.003, 0.005, 0.010 and 0.020 *M* strength run between initial and final periods	For values for solubilities in salt solutions see Table II		
Final period	No. of detns.	15	6	
	Mean value of single detns.	4.50	4.62	4.56
Final av. of first series				4.58

SECOND SERIES

		Cell 2	Cell 3	Av.
Initial period	No. of detns.	4	5	
	Mean value of single detns.	4.57	4.66	4.62
Salt period	NaCl solns. of 0.015 and 0.20 *M* strength	For values for solubilities in salt solutions see Table II		
Final period	No. of detns.	4	3	
	Mean value of single detns.	4.59	4.57	4.58
Final av. of second series				4.60

TABLE I (*Concluded*)

THIRD SERIES

		Cell 1	Cell 4	Av.
Initial period	No. of detns.	4	5	
	Mean value of single detns.	4.67	4.66	4.66
Salt period	NaCl solutions of 0.001, 0.003, 0.005, 0.010 run between initial and final periods	For values for solubilities in salt solutions see Table II		
Final period	No. of detns.	3	4	4.56
	Mean value of single detns.	4.52	4.59	
Final av. of third series				4.61

In Table II are recorded the determinations with sodium chloride solutions as solvents. The values in each series are averages of about six single determinations.

TABLE II

SOLUBILITY OF LUTEOCOBALTIC-HEXACYANO-COBALTIATE IN SODIUM CHLORIDE SOLUTIONS AT 18°

	10^5				
M_{NaCl}	$s_1 \cdot 10^5$	$s_2 \cdot 10^5$	$s \cdot 10^5$	$5 + \log s$	$10^2\sqrt{\mu}$
0.000	1.375	1.375	1.375	0.138	1.11
.001	1.69	1.73	1.71	.233	3.40
.003	2.11	2.11	2.11	.324	5.65
.005	2.42	2.49	2.455	.390	7.23
.010	3.02	3.22	3.12	.494	10.02
.015	4.02	3.83	3.93	.594	12.39
.020	4.41	4.70	4.56	.659	14.28

s_1 corresponds to the first series, s_2 to the second and third. s is the mean value of s_1 and s_2. In the last column is given the square root of the ionic strength[3] which in the present case is expressed by $\mu = M_{NaCl} + 9s$. The table shows the extraordinary effect of the added salt; 0.001 M sodium chloride increases the solubility by 25% in comparison with pure water.

Discussion

In Fig. 1 log s is plotted as ordinate against the square root of the ionic strength. This graph up to $\sqrt{\mu} = 0.07$ comes out exactly as a straight line, the slope being 4.14. By means of the relation between solubility and activity coefficient[4] this result may be stated as

$$-\log f_3 = 4.14\sqrt{\mu} \tag{1}$$

where f_3 is the activity coefficient of a tervalent ion. From the above equation the following values are calculated for f_3 for saturated solutions of the luteo salt.

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[3] Lewis and Randall, THIS JOURNAL, **43**, 1112 (1921).

[4] Brönsted, *ibid.*, **42**, 761 (1920).

Table III

Activity Coefficient of Tervalent Ions

M_{NaCl}	0.000	0.001	0.010
f_3	.901	.723	.386

In spite of the extreme dilution of the water solution, 1.375×10^{-5} moles per liter, the activity coefficient of the tervalent ion is nevertheless 0.9, that is, differing by 10% from the value in the ideal region where no interionic forces are operating. Even in a solution so dilute as 10^{-7} molal, f_3 will be 1% less than unity. In 0.001 N sodium chloride where $\sqrt{\mu}$ is chiefly determined by the sodium chloride the activity coefficient of a tervalent ion has decreased to 0.723. In 0.01 N sodium chloride where $\sqrt{\mu}$ is practically completely dependent upon sodium chloride, the activity coefficient has been reduced to 0.386. In contrast to these values the corresponding values for a univalent ion are 0.97 and 0.90, respectively.

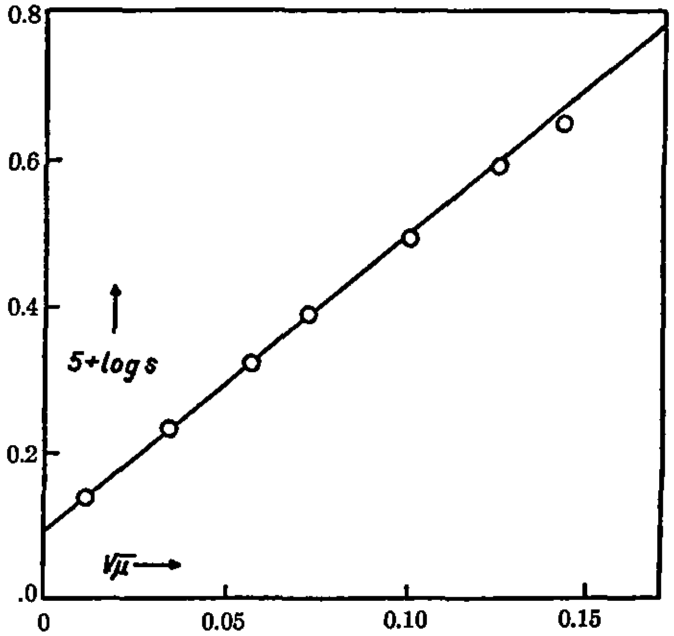

Fig. 1.

The most interesting aspect of the present investigation is its application to the Debye-Hückel theory.[5] The theoretical equation can be reduced to the following simple form.[1]

$$-\log f = 0.5z^2\sqrt{\mu} \tag{2}$$

where z is the valence of the ion having the activity coefficient f. In the present case $z = 3$.

Writing the numerical factor of Equation 1 as $4.14 = 0.46 \times 3^2$ and inserting this value in the empirical equation, we have

[5] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

$$-\log f_3 = 0.46 \times 3^2 \sqrt{\mu} \tag{3}$$

This shows a striking concordance between theory and experiment. The agreement is especially important because of first, the extreme dilution to which the experiments are extended, second, the high valence of both ions whose activity coefficients are considered and, third, the alteration in type of the saturated solution from tervalent to practically uni-univalent as the ionic strength is increased.

In the work of Brönsted and La Mer on salts of lower valence types, it was found that the numerical values approached the theoretical value, 0.50, somewhat more closely. Some of the recent experimental material[6] including that of the present investigation indicates a slightly lower value. Even if this conclusion is not of obligatory nature it seems by no means impossible, nevertheless, that there is enough uncertainty in the basis of the theoretical constant to account for a deviation of 10% or more.[7]

Summary

The solubility of the tervalent salt luteocobaltic-hexacyano-cobaltiate, $(Co(NH_3)_6)Co(CN)_6$, was directly determined in sodium chloride solutions ranging in concentration from 0 to 0.02 *N*. In this region the solubility changes from 1.38×10^{-5} to 4.56×10^{-5} at 18°.

The data obtained exhibit a marked concordance with the requirements of the electrolytic theory of Debye and Hückel.

Copenhagen, Denmark

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[6] Randall and Vanselow, This Journal, 46, 2418 (1924). Noyes and Baxter, *ibid.*, 47, 2122 (1925).

[7] The uncertainty of the value of the constant theoretically calculated is indicated by the fact that temperature coefficients of activity coefficients cannot be derived with satisfactory accuracy by using it. That is, the formula $\log_{10} f = 1.80 \times 10^6 (DT)^{-3/2} z^2 \sqrt{\mu}$ to which the general activity equation of Debye and Hückel can be reduced for great dilution does not harmonize with the formula for the temperature coefficient $d \ln f/dT = U/RT^2$ [compare Brönsted, *Z. physik. Chem.*, 100, 139 (1922)] when the numerical values of D, T and U are introduced. Further discussion of this point will be reserved, however, for a later publication.

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THE IONIZATION POTENTIAL OF METHANE

BY GEORGE GLOCKLER[1]

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The ionization potentials of several hydrocarbons have been determined by Hughes and Dixon[2] and by Boucher.[3,4] These investigators found that these ionization potentials are all in the neighborhood of 10 volts. At present it is believed that the ionization potential of a molecule corresponds to the removal of an electron from the molecule and therefore to the production of a mole-ion, rather than to dissociation of the molecule and ionization of one of the parts.

In this research we have determined the ionization potential of methane by the usual methods of electron impact and have found it to be between 14.4 and 15.2 volts. We have further predicted this quantity from Eve's rule.[5] Our prediction is based on the belief that methane has a rare-gas structure and that the reaction leading to ionization consists in the removal of an electron, in accordance with the equation $CH_4 = CH_4^+ + E^-$.

The Physical Properties of Methane.—The belief that methane has the rare-gas arrangement of electrons is readily justified. When a comparison is made of the physical properties of methane and the rare gases, which are not dependent on molecular weight, it is seen from Table I that methane fits in between argon and krypton. We shall also see from this investigation that the ionization potential of methane lies between the ionization potentials of argon and krypton.

TABLE I

COMPARISON OF PHYSICAL PROPERTIES OF THE RARE GASES AND METHANE

Property	Ne	A	CH_4	Kr
Critical temperature, °K.	44.40	150.66	190.1	210
Critical pressure, atm.	26.86	47.99	54.9	54.3
van der Waals' constant, $a \times 10^5$	42.2	268	449	462
van der Waals' constant, b, cm.^{3}	17.0	32.2	35.6	39.6
Radius from critical data, Å.	1.19	1.47	1.56	1.58
Molecular refractivity P_D in cm.^{3}	1.0	4.18	6.36	10.2
Ionization potential, volts	21.5	15.4	14.4–15.2	13.3

Another interesting property which shows the similarity of methane and argon most strikingly is the mean free path of electrons in these gases. The curves connecting the mean free path of electrons in the rare gases

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[1] National Research Fellow in Chemistry.

[2] Hughes and Dixon, *Phys. Rev.*, 10, 495 (1917).

[3] Boucher, *ibid.*, 19, 189 (1922).

[4] For a summary see *Nat. Res. Council Bull.*, No. 48, 123 (1924).

[5] Eve, *Nature*, June 30, 1921.

and their energies are known from the work of Ramsauer.[6] The curves for methane and argon are identical in shape, while the curve for neon differs from that obtained for methane.[7,8] The theory of this phenomenon has been given by Zwicky.[9]

The Predicted Ionization Potential.—Eve's rule states: "The product of the ionization potential of an atom and its radius is a constant." This rule is not an exact one, but it serves well when applied to the rare gases, and we have used it to predict the ionization potential of niton,[10] and now we wish to apply it to methane. It may be questioned whether or not this rule can be applied to molecules. It is certainly believed at present that methane has the rare-gas arrangement of its outer electrons. This belief is the very foundation of our modern theory of chemical combination as advanced by G. N. Lewis.[11] We may, therefore, plot the ionization potential of the rare gases as determined by Hertz[12] against their kinetic-theory diameters obtained from critical data on viscosity, and obtain the curve shown in Fig. 1. The predicted ionization potential of methane is 13.7 volts.

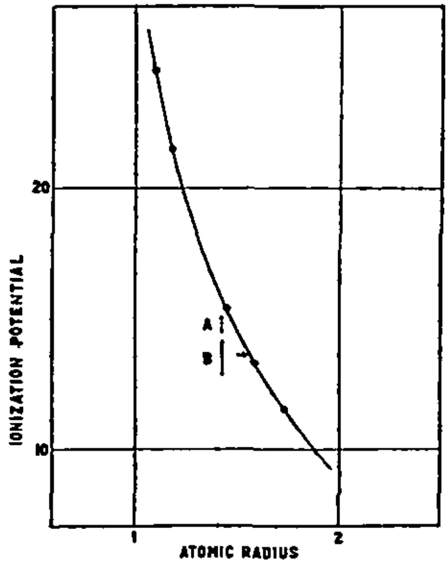

Fig. 1.—Ionization potentials in volts, plotted against atomic radii in Ångström units. *A*, experimental value, and *B*, predicted value of the ionization potentials.

Table II

Comparison of Radii and Ionization Potentials

Gas	Radii, Å. From viscosity	Radii, Å. From critical data	Ionization potential Volts	Eve's constant
He	0.94	1.13	24.5	25.4
Ne	1.18	1.19	21.5	25.5
A	1.42	1.42	15.4	21.8
Kr	1.56	1.59	13.3	20.8
Xe	1.74	1.71	11.5	19.9
CH_4	1.56	1.57	(13.7)	21.4

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[6] Ramsauer, *Ann. Physik*, **64**, 513 (1921).

[7] Glockler, *Proc. Nat. Acad.*, **10**, 155 (1924).

[8] Brode, *Phys. Rev.*, **25**, 636 (1925).

[9] Zwicky, *Phys. Z.*, **24**, 171 (1923).

[10] *Phil. Mag.*, **50**, 997 (1925).

[11] Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., 1923.

[12] Hertz, *Z. Physik*, **31**, 463 (1925).

The Experimental Value of the Ionization Potential.—The Lenard method was used to determine the ionization potential. Full description of the method is found in several places.[4] The experimental tube used is described by Hertz[13] and is shown in Fig. 2. We shall mention only the points to which particular attention has been paid in order to work with methane.

Methane was prepared from the gas issuing from the gas wells of the Midway Gas Company at Taft, California. The gas is said to be 98% methane. It was purified by fractional distillation at liquid-air temperatures. We wish to thank the Midway Gas Company for the supply of methane.

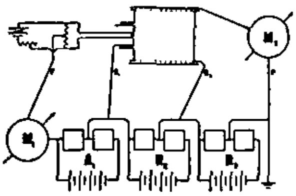
Fig. 2.—Wiring diagram.

It is important to avoid thermal decomposition of the gas by the hot filament. It is known[7] that a calcium-oxide covered platinum filament does not cause decomposition if used at a low temperature. Furthermore, in our experiments the pressure was always measured at the beginning and end of a run, and it was found that no change of pressure resulted during an experiment. If the hot filament had decomposed the gas according to the equation $CH_4 = 2H_2 + C$, an increase in pressure would have occurred. Since the pressure did not increase, we believe that this reaction did not take place.

Helium was used as a calibrating gas, and the experiments were performed in a mixture of helium and methane. In Table III are given the data of eight experiments.

Table III

Experimental Data on the Ionization Potential of Methane

Pressure in mm. of Hg					Point where current first rises (Fig. 3)	Large rise in current
CH_4	He	Total	Total press / CH_4 press.	Liq. air	Volts	(Fig 3) Volts
0.031	0.249	0.280	9.1	No	14.45	15.35
.036	.203	.239	6.6	No	14.70	15.10
.021	.189	.210	10.0	No	14.80	15.25
.040	.252	.292	7.3	No	14.30	15.05
.039	.227	.266	6.7	No	14.13	14.88
.044	.283	.327	7.4	No	14.20	14.92
.031	.233	.264	8.6	Yes	14.25	15.35
.030	.157	.187	6.2	Yes	14.12	15.31
				Av.	14.4	15.2

A retarding field of 2.0 volts was applied in the second condenser (G_1-G_2 in Fig. 2) to help the positive ions diffuse to the plate and a large retarding field of 30 volts in the third condenser (G_2-P in Fig. 2) prevented the electrons from the filament from reaching the plate. The filament carried 4.5 amperes at a drop of 1.4 volts.

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[13] Hertz, *Proc. Roy. Soc. Amsterdam*, 25, 179 (1922).

Discussion of Results.—It may be questioned whether we have actually determined the ionization potential of methane or a radiation potential since the rise in positive current to the plate might be due to photo-electrons, and then we would be measuring a radiation potential. However, the rise in positive current is large compared to the photo-currents usually obtained in such experiments, although the curve in helium alone does show a large current rise at the radiation potential near 20 volts. It is, of course, well known that the methods of critical potentials must be combined with the methods of mass-spectroscopy, in order to make sure at what voltage positive ions actually occur. But combining our results with the prediction from Eve's rule, it seems reasonably certain that we have actually measured the ionization potential. Furthermore, we do not find a second rise in current in pure methane after 14.4 volts, as we have found in pure helium at 24.5 volts and, this fact also is in favor of the view that ionization in methane sets in near 15 volts. The positive current actually starts to rise at 14.4 volts and, as usual, we have a small rise in current in a region of 0.8 volt (between 14.4 and 15.2 volts). This may be due to the velocity distribution of the impinging electrons and to efficiency of impact. However, in our calibration we have taken the point where the current *first* rises due to helium impacts, and it might seem more reasonable to have taken the *first* appearance of positive current (14.4 volts) as the ionization potential. We may certainly say from our experiments that methane has a *critical* potential between 14.4 and 15.2 volts, and that this is presumably the *ionization* potential.

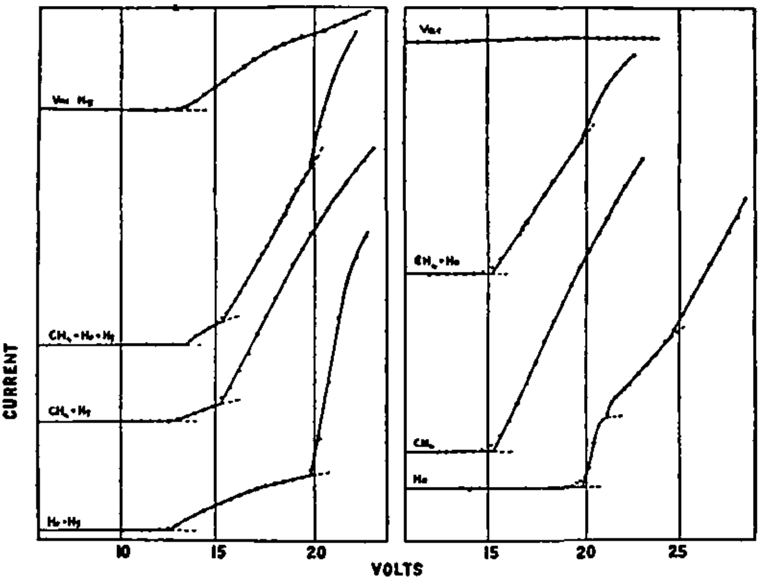

Fig. 3.—Current-potential curves in methane, helium and methane-helium mixture, with liquid-air trap off and on.

If we compare this result with the measurements of others[2] we find that our value is much higher. From Fig. 3 it is seen that when mercury vapor is present (no liquid air) the current rises at about 12 volts. This rise in positive current must be due to ionization of mercury vapor, because we can also obtain it in an ordinary vacuum, and it does not occur when the mercury vapor is removed by means of liquid air. However, the ionization potential of mercury is known to be 10.4 volts, so that positive mercury ions should appear at that voltage. They may appear in our apparatus at 12.0 volts because at the small vapor pressure of mercury at room temperature (0.001 mm.) only a few mercury ions are produced at 10.4, and only at 12.0 volts are enough ions produced to be measured by our galvanometer. The appearance of positive current depends then on the gas pressure used, the efficiency of ionization, and the sensitivity of the galvanometer used. In the case of methane and helium we believe we had a high enough pressure to detect the rise in positive current very near to the critical potentials, because the pressures of helium and methane in the mixtures used are of the same order of magnitude, and we know from the work of Hughes and Klein[14] and Dymond[15] on the efficiency of ionization of methane and excitation of helium that the former is much larger than the latter. If, therefore, we can detect the resonance potential of helium, we feel sure that the same apparatus will show the critical potential of methane at approximately the correct voltage.

We therefore believe that the lower results in the earlier experiments on methane have possibly been due to mercury vapor.

Referring now to Fig. 1 we see that the predicted value of the ionization potential and the experimental value check satisfactorily. Therefore, we believe that it is not unreasonable to take this agreement as additional experimental proof of the rare-gas structure of methane. On our modern view of atomic structure[11] we should believe that methane is like neon. Grimm[16] has brought out this relation very strikingly. He considers methane as a pseudo-atom of neon, since the carbon and hydrogen nuclei together have the total atomic number of ten, as has neon. In neon, however, the total charge is situated at one point while in methane the positive carbon center (the carbon atom with its two K-electrons) and the four protons take up a larger volume. We must, therefore, expect that the methane molecule is larger than the neon atom and that its ionization potential is less than the ionization potential of neon. We see that methane is more like argon in size and that their ionization potentials are very nearly equal. We should, therefore, be inclined to draw the electron orbits in methane so as to include the hydrogen nuclei rather than to imagine that

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[14] Hughes and Klein, *Phys. Rev.*, 23, 460 (1924).

[15] Dymond, *Proc. Roy. Soc.*, 107A, 291 (1925).

[16] Grimm, *Z. Elektrochem.*, 31, 474 (1925).

pairs of electrons are situated between the carbon center and the hydrogen nuclei. This makes the methane molecule more rare-gas-like when looked at from a distance.

In conclusion we wish to thank Professor R. C. Tolman for the interest he has shown in this research.

Summary

We have measured a critical potential in methane at 14.4–15.2 volts, which we believe to be the ionization potential. Using Eve's rule we have predicted the ionization potential to be 13.7 volts. Special attention has been paid to the possible thermal decomposition of the gas by the hot filament, and it has been avoided. We have also taken care of the effect of mercury vapor in interpreting our current-potential curves.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 174]

ELECTROMOTIVE-FORCE MEASUREMENTS IN AQUEOUS SOLUTIONS OF HYDROCHLORIC ACID CONTAINING SUCROSE[1]

BY GEORGE SCATCHARD

RECEIVED MARCH 4, 1926 PUBLISHED AUGUST 5, 1926

Solutions of sucrose in water have long occupied a prominent position in the study of the properties of solutions, and particularly in the study of reaction rates. With the correlation of reaction rates with activities, electromotive-force measurements in solutions containing sucrose have become important. All the measurements so far reported, however, have been made in cells containing liquid junctions, and with those junctions made by dipping a small tube containing the lighter liquid into a larger one containing the heavier. Most of them have been made with a hydrogen electrode.

This paper describes an attempt to study the problem in more detail by dividing it into two parts: a study of the effect of sucrose on the liquid-junction potential between hydrochloric acid and saturated potassium chloride, and a study of the effect of sucrose on the potential of the hydrogen electrode. The measurements do not agree with those in the literature, and they disclose three sources of errors which probably account for the discrepancies. They give a more precise knowledge of the ion activities in sucrose solutions, and they comprise the first experimental study, so far as I am aware, of the effect of a non-electrolyte solute on liquid-junction potentials.

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[1] Reported to the Physical-Inorganic Division of the American Chemical Society at Los Angeles, August 7, 1925. The experimental work was carried out in 1924 during the tenure of a National Research Fellowship.

Cells with Liquid Junctions

The electromotive force at 25° of the cell Hg | HgCl, KCl (satd.) | HCl (c_1), sucrose (c_2), AgCl | Ag was measured in the flowing-junction apparatus previously described,[2] which gives a continuously renewed junction of large cross section but of almost knife-edge thinness, and which also permits a study of the effect on the liquid-junction potential of interdiffusion of the two solutions without the disturbance of turbulent mixing. The concentration of hydrochloric acid was kept constant at 0.1012 mole per liter, while that of sucrose was varied from zero to 700 g. per liter. All weights are reduced to vacuum.

The sucrose had been precipitated with alcohol, dried in a vacuum at 50°, and then in a current of dry air at the same temperature.[3] The other materials were all prepared as for the earlier studies.[2,4] The silver chloride electrodes were all prepared in the solution without sucrose and then washed several times in the solution in which they were to be used. Only two measurements, with a single filling of the apparatus, were made with each solution. Otherwise the procedure was the same as that described in the papers cited.

TABLE I

ELECTROMOTIVE FORCE OF THE CELL Hg | HgCl, KCl (satd.) | HCl (0.1012 *N*), sucrose, AgCl | Ag

Sucrose, g. per liter	*E* flowing	Dev. from mean	*E* maximum	Dev. from mean
0.00	0.0431	0.0000_6	....	....
.00	.0431	$.0000_1$	0.0435	0.0000_4
98.42	.0414	$.0000_3$	.0418	$.0000_3$
99.71	.0410	$.0000_4$	.0412	....
200.66	.0390	$.0000_6$	.0394	....
301.13	.0368	$.0000_6$	.0376	....
406.88	.0344	$.0000_6$	.0351	....
489.86	.0303	$.0000_3$	.0312	....
605.67	.0251	$.0002_3$	.0265	....
700.38	.0195	$.0002_7$	.0224	$.0001_9$

The measurements with a flowing junction are given in the second column of Table I, and the maximum values after the flow is stopped in the fourth column. It was noted in the earlier paper that the electromotive force of a similar cell, but with no sucrose, increases 0.3 mv. when the flow is stopped, and that the amount of this change is independent of the acid concentration.[5] When sucrose is added to the acid this difference increases to 3.0 mv. for the solution containing 700 g. per liter, and the

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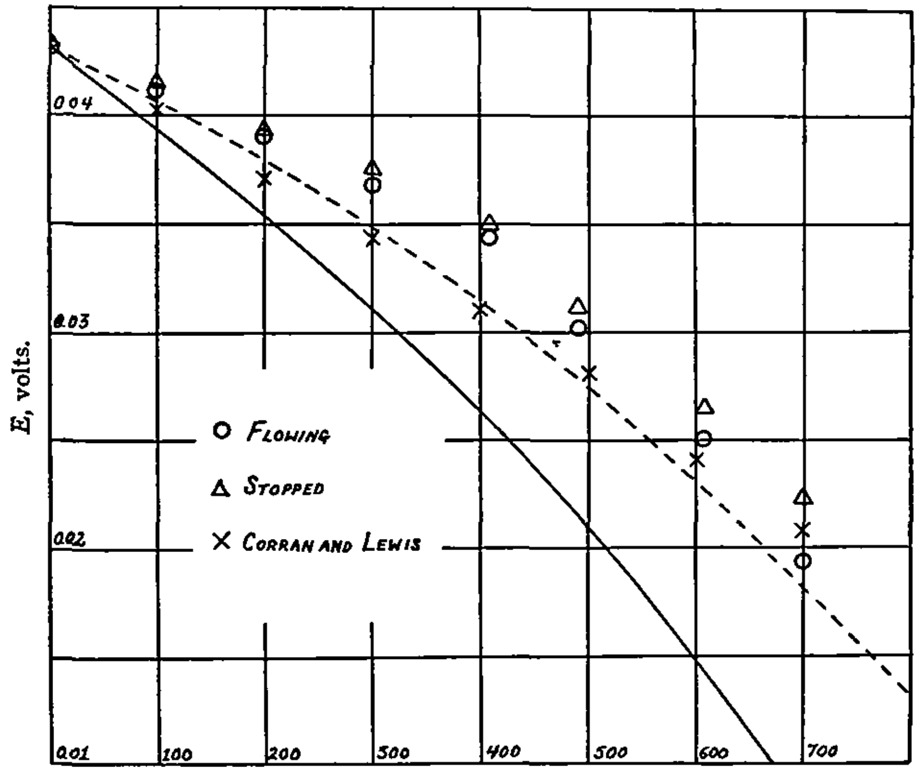
[2] Scatchard, THIS JOURNAL, 47, 696 (1925).

[3] I wish to thank Professor H. A. Fales of Columbia University for the gift of the sugar used.

[4] Scatchard, THIS JOURNAL, 47, 641 (1925).

[5] See correction, *ibid.*, 47, 3107 (1925).

time required to reach the maximum value is not changed. Although this effect makes the readings with the solutions flowing more erratic and sensitive to the rate of flow, it is not difficult to fix the average value to 0.1 mv., as the small deviations from the mean values show. However, since the difference between the potentials at two types of junction changes, one at least of the potentials must also change. It is probable that both potentials change in the same direction, perhaps by several millivolts, but there is no indication of the direction of this change. Since one millivolt in the potential of this cell corresponds to a 4.5% change in activity, it is apparent that the uncertainty in activity values determined with the use of a liquid junction must be large.



Grams of sucrose per liter.

Fig. 1.—Hg | HgCl, KCl (satd.) | HCl (0.1012 *N*), sucrose, AgCl | Ag. Broken line, $\sqrt{A_H \times A_{Cl}}$. Full line, $\sqrt{A_K \times A_{Cl}}$.

In Fig. 1 the values of the electromotive force with flowing junction are represented by circles, and the maximum values without flow by triangles. The measurements of Corran and Lewis[6] on the cell Ag | AgCl, HCl (0.5 *N*) | KCl (satd.) | HCl (0.1 *N*), sucrose, AgCl | Ag, plus a constant to give agreement in the solution without sucrose, are represented by the crosses. The curves in this figure will be discussed in a later section.

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[6] Corran and Lewis, This Journal, 44, 1673 (1922).

Part of the difference between my measurements and those of Corran and Lewis may be attributed to the fact that their saturated potassium chloride bridge contained sucrose in concentration about half that in the acid solution.

It is probable that the electromotive force of this cell, as of those to be discussed later, changes somewhat as the sucrose is inverted. The effect should be small during the short time required for measurement, and not greater than the deviation from the mean of the individual values. It is probably responsible for the fact that the deviations are larger for the last two solutions, but no attempt was made to study it quantitatively, or to correct the measured values for it.

Cells Without Liquid Junction

The electromotive force at 25° of the cell Pt, H_2 | HCl (c_1), sucrose (c_2), AgCl | Ag was measured with the Clark type rocking hydrogen electrode previously described.[4] The solutions and silver chloride electrodes were prepared with those used in the cells with liquid junction. On each solution two measurements were made with different hydrogen electrodes but with the same silver chloride electrode. For reasons to be discussed below it was necessary to continue the rocking of the hydrogen electrode while the measurements were made. Otherwise the technique was the same as that described in the earlier paper. Measurements were also taken after the rocking had ceased for a definite time, and in some cases with the electrode stationary but with hydrogen bubbling through the solution.

Since the completion of these experiments Taylor and Bomford[7] and Pennycuick[8] have noted that the electromotive force of the cell with a hydrogen electrode and a saturated potassium chloride bridge changes during the inversion of sucrose in the direction indicating an increasing activity of the hydrogen-ion. The electromotive force of this cell changes similarly. The change was studied only with the solution containing 700 g. per liter. In the other solutions the change is much smaller and negligible for the short times between the mixing of the solutions and the measurements.

For the most concentrated solution the change for complete inversion is about 10 mv. From the rate of inversion measured by Moran and Lewis[9] this should give a change of about 0.01 mv. per minute at the start of the reaction. The measurements during the course of the reaction and the calculated values at the time of mixing are given in Table II.[10] Part of

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[7] Taylor and Bomford, *J. Chem. Soc.*, **125**, 2016 (1924).

[8] Pennycuick, This Journal, **48**, 6 (1926).

[9] Moran and Lewis, *J. Chem. Soc.*, **121**, 1613 (1922).

[10] The values at the time of mixing depend somewhat upon the assumption as to the functional relationship between the electromotive force and the fraction of the sugar inverted. If the change in electromotive force is due to a change in the total number of moles, the activity of the ions should be (approximately) a linear function of the

the irregularity shown in the table may be due to the fact that the temperature, except at the time of the electromotive-force measurements, was not accurately controlled.

TABLE II

EFFECT OF REACTIONS ON POTENTIAL IN SOLUTIONS CONTAINING 700 G. OF SUCROSE PER LITER

Expt.	Time, min.	% Inverted	Reading, volts	Average variation from mean	Reading corr. to zero time
A	102–114	13.9	0.3044	0.0000_1	0.3059
	116[a]	..	.3032	....	....
B	164–179	21.2	.3017	$.0000_2$	.3044
	447–460	46.6	.2997	$.0000_1$	.3054
C	505–517	50.6	.3003	$.0000_0$	.3064
	1500–1512	87.5	.2964	$.0000_4$	.3054
	1515[a]	..	.2957	....	....
				Av.	.3055

[a] Rocking stopped immediately after last reading.

The measurements indicate that another chemical action is taking place at the hydrogen electrode. When the shaking was stopped the electromotive force decreased at the rate of 0.1–0.7 mv. per minute. The rate of decrease appeared nearly independent of the sucrose concentration, but varied greatly with some factor not controlled in these experiments. It was always many times the change due to inversion. When the shaking was resumed the electromotive force rose rapidly to its former value. Bubbling hydrogen around the electrode without shaking gave a steady value somewhat lower than that obtained when the cell was shaken. This behavior indicates clearly a reaction that uses up hydrogen and keeps the solution at the electrode unsaturated. The degree of unsaturation depends upon a balance between the rate of this reaction and the rate of diffusion to the electrode, and therefore upon the thickness of the diffusion layer. With the rocking electrode the diffusion layer is so thin that the error is probably small. The thicker diffusion layer with a bubbling electrode leads to a lower electromotive force. In either case the diffusion layer remains so nearly constant that the disturbance could not be detected with a single type of electrode. With neither bubbling nor rocking, the diffusion layer thickens continually as the reaction progresses so that the electromotive force is not constant. Examples of the change when the rocking is stopped are given by the rows marked *a* in Table II.

The most probable reaction that would use up hydrogen is the hydrogenation of sucrose or of the products of its inversion catalyzed by the platinum black of the electrode. A disturbance due to this reaction has

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fraction inverted; if the change is due to a change in the dielectric constant, the electromotive force should be a linear function. These two assumptions lead to average values which differ by about 1 mv. Probably both factors are operating. The values given in the table are averages for the two assumptions.

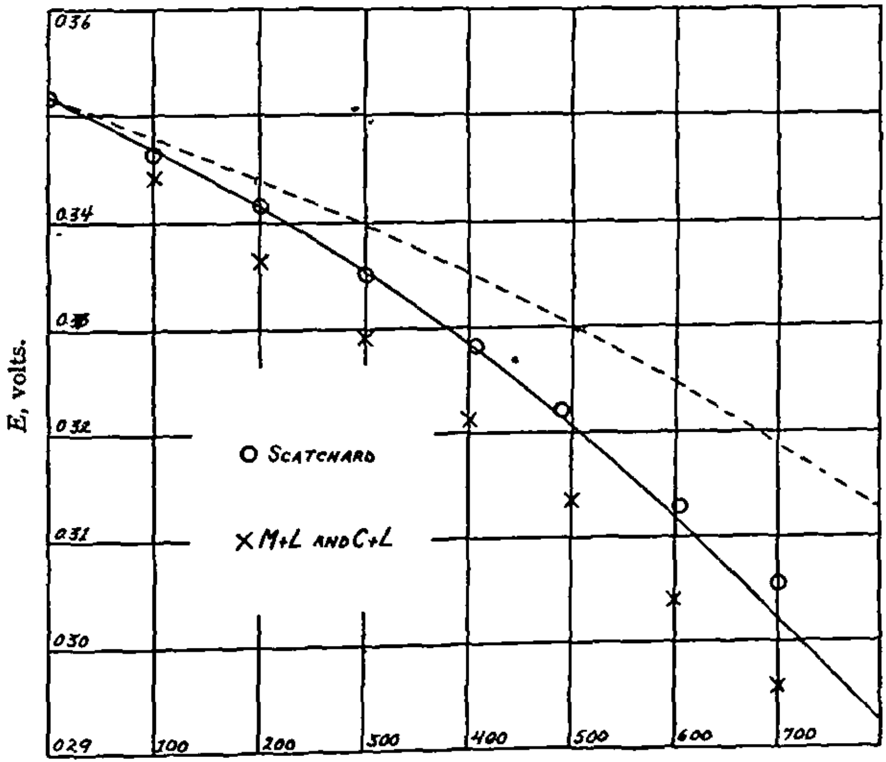
not previously been recorded, probably because all the earlier measurements have been made with bubbling electrodes only. I can find no record of a chemical study of this reaction, although the reaction of the sugars with oxygen in the presence of platinum black has long been known.

Table III

Electromotive Force of the Cell Pt, H_2 | HCl (0.1012 *N*), sucrose, AgCl | Ag

Sucrose, g. per liter	E meas.	Dev from mean	E calcd.	d^{2}_{4}	a_{w} without acid	Dielectric constant
0.00	0.3516	0.0001_1	0.3518	0.9986	1.0000	78.8
.00	.3518	$.0000_1$	.3518	.9986	1.0000	78.8
98.42	.3466	$.0001_3$	.3473	1.0364	0.9944	76.3
99.71	.3461	$.0002_3$	.3472	1.0369	.9943	76.3
200.66	.3412	$.0000_5$	.3413	1.0752	.9874	74.3
301.13	.3352	$.0000_2$	.3350	1.1131	.9789	72.3
406.88	.3283	$.0000_0$	.3276	1.1526	.9676	70.1
489.86	.3222	$.0000_6$	.3211	1.1846	.9565	68.3
605.67	.3129	$.0001_0$	.3110	1.2245	.9363	65.7
700.38	.3055	$.0005_5$	.3018	1.2623	.9143	63.4

The results for the cells without liquid junction are given in the second column of Table III, and are shown graphically by the circles in Fig. 2.



Grams of sucrose per liter.

Fig. 2.—Pt, H_2 | HCl (0.1012 *N*), sucrose, AgCl | Ag. Broken line, no hydrate; full line, hydrate.

No attempt was made to correct any but the last for the effect of inversion, but the error from this cause should not be greater than twice the deviation from the mean given in the third column. The sum of the measurements of Corran and Lewis[6] on the cell Ag, AgCl, HCl (0.5 N) | KCl (satd.) | HCl (0.1 N), sucrose, AgCl | Ag and those of Moran and Lewis[9] on the cell Pt, H_2 | HCl (0.1 N), sucrose | KCl (satd.) | KCl (1.0 N), HgCl | Hg should give the same change on the addition of sucrose as the cell without liquid junction if their liquid junctions are reproducible. Their results, with a constant added to give agreement for the solution without sucrose, are represented by the crosses in Fig. 2. The discrepancy is several millivolts.

Theoretical Interpretation

The electromotive force of the cell Pt, H_2 | HCl, AgCl | Ag in any solvent mixture whose average molecular weight, dielectric constant and vapor pressure of water are known may be calculated from the Debye theory of electrolytic solutions. The methods of calculation and the necessary assumptions are given elsewhere.[11] The water activity was determined by interpolating for concentration the values already interpolated for temperature[12] from the measurements of Berkeley, Hartley and Burton.[13] The dielectric constants were determined by interpolation from a smooth curve drawn through the values of Debye and Sack,[14] assuming that for each solution the ratio of the dielectric constant to that of water is the same at 25° as at 18°. These results agree excellently with those of Harrington[15] on dilute solutions if the latter are multiplied by 1.027 to make his dielectric constant of water agree with that of other observers. The measurements of Drude[16] at higher concentrations do not agree so well, and those of Fürth[17] are very different throughout the whole concentration range.[18] The density, water activity in the solution without acid and the dielectric constant for each solution are given in Table III.

If the mole fraction of the ions be calculated on the assumption that the sucrose and water do not react chemically, the agreement between the theory and measurements is poor. The curve for this case is shown by the broken line in Fig. 2. It has been shown,[19] however, that the vapor

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[11] Scatchard, THIS JOURNAL, 47, 2098 (1925).

[12] Scatchard, *ibid.*, 45, 1580 (1923).

[13] Berkeley, Hartley and Burton, *Phil. Trans.*, 218A, 295 (1919).

[14] Private communication.

[15] Harrington, *Phys. Rev.*, 8, 581 (1916).

[16] Drude, *Z. physik. Chem.*, 23, 267 (1897).

[17] Furth, *Ann. Physik*, 70, 63 (1923); *Physik. Z.*, 25, 676 (1924).

[18] Recent measurements of Kackel [*Ann. Physik*, 77, 417 (1925)] are generally somewhat lower, with a maximum difference of 1% from the values quoted.

[19] Scatchard, THIS JOURNAL, 43, 2406 (1921).

pressure of aqueous sucrose solutions may be simply and accurately explained by assuming that there is hydrate formation and that the vapor pressure of water is proportional to the mole fraction of the uncombined water. With these assumptions the number of moles of water per liter is equal to the number of moles of sucrose multiplied by the activity of the water and divided by one minus this activity. The values calculated with this assumption are represented by the full curve of Fig. 2 and are given in Col. 4 of Table III. The agreement between measurement and theory is very much better. The deviations in concentrated solutions increase regularly and are in the direction to be expected from the fact that the theory neglects the effect of the acid on the equilibrium between sucrose and water.

The theory includes four reasons why the electromotive force should change with a change in the concentration of sucrose: the change in mole fraction due to the change in the total number of moles per liter; the change in the free-energy increase of the reaction $H_3O^+ = H^+ + H_2O$ due to the change in the activity of the water; the effect of the change in dielectric constant on the activity at infinite dilution; and the effect of the change in dielectric constant on the activity coefficient. Table IV shows the magnitude of each of these effects for the most concentrated solution, and shows also the effect of the two assumptions regarding the total number of moles.

TABLE IV

FACTORS IN EFFECT OF SUCROSE ON ELECTROMOTIVE FORCE (700 G. PER LITER)

	HCl		KCl	
Factor	Hydrate	No hydrate	Hydrate	No hydrate
Mole fraction	−0.0429	−0.0263	−0.0429	−0.0263
Water activity	− .0023	− .0023	.0000	.0000
E_N *(inf. dil.)*	− .0088	− .0088	− .0327	− .0327
Activity coeff.	+ .0040	+ .0040	+ .0052	+ .0052
Total change	− .0500	− .0334	− .0704	− .0538

The electromotive force of the cell Ag \| AgCl, KCl (0.1012 *N*) \| K, Hg \| KCl (0.1012 *N*), sucrose (*c*), AgCl \| Ag was calculated in an exactly similar way, and the effects of the four factors for the most concentrated solution are shown in Table IV. If the addition of sucrose affected the activity of the potassium and chloride ions to an equal extent and did not change the liquid-junction potential, the change in electromotive force of the cell Hg \| HgCl, KCl (satd.) \| HCl (0.1012 *N*), sucrose (*c*), AgCl \| Ag would be half the electromotive force of the above cell. This corresponds to the full curve of Fig. 1. The assumption of equal effect on the potassium and chloride ions demands a change in the liquid-junction potential of more than ten millivolts, which seems improbable. The measurements are fitted much better by assuming that the change in activity of the chloride ion is equal to the change in the mean activity of the ions of hydrochloric acid, represented by the broken line in Fig. 1. These results confirm the conclusions drawn from measurements on alcohol-water mixtures[11] that the effect of changing dielectric constant on activity cannot be the same for the potassium and the chloride ions, but the uncertainty as to the liquid-junction potential prevents more precise conclusions.

Discussion

In spite of the difficulties of measurement it is believed that the measurements on the cell without liquid junction are accurate to a few tenths of a millivolt when the sucrose concentration is not greater than 500 g. per liter, and to a few millivolts for higher concentrations. This corresponds to an accuracy in the measurement of the mean activity of the ions of hydrochloric acid of about 0.5% below 500 g. per liter, and to a few per cent. above. The agreement with the theory is not quite so close, but it is as good as should be expected from the simplifying assumptions which were made.

The measurements with the cell with flowing junction are reproducible to the same precision, but their interpretation in terms of activities are uncertain to several millivolts on account of the lack of knowledge of the effect of sucrose on the liquid junction potential. Moreover, in this case theory gives no definite values with which the measurements might be checked. So the values of single ion activities in solutions containing sucrose are uncertain to many per cent., and it is evident that this uncertainty cannot be reduced without some radical improvement in experimental technique or in theoretical knowledge.

The values previously reported in the literature for the activity of the hydrogen ion in sucrose solutions are even more uncertain because they are probably not free from error due to irreproducible liquid-junction potentials and to the effect of the hydrogenation reaction on the potential at a bubbling hydrogen electrode. The new experimental evidence is thus directly contradictory to the conclusions which I drew elsewhere[12,20] that these values might be accepted as accurate.

This uncertainty as to the activity of the hydrogen ion in solutions containing sucrose makes inconclusive the attempts made by myself,[12,21] and others[9,22] to determine the mechanism of the inversion process by fitting the rates of reaction quantitatively with formulas containing this hydrogen activity. Even the difference between the change of liquid junction potential with flowing and with stationary junction amounts to 11% in the hydrogen activity between 0 and 700 g. of sucrose per liter, while the change in water activity in this range is less than 9%. Obviously the number of moles of water that enter into the reaction cannot be accurately determined.

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[20] Scatchard, This Journal, 45, 1716 (1923).

[21] Scatchard, *ibid.*, 43, 2387 (1921).

[22] Jones and Lewis, *J. Chem. Soc.*, 117, 1120 (1920).

Summary

The electromotive forces of the cell Hg | HgCl, KCl (satd.) | HCl, sucrose, AgCl | Ag with flowing junction and of the cell Pt, H_2 | HCl, sucrose, AgCl | Ag have been measured at 25° with 0.1012 *N* acid and sucrose concentrations ranging from 0 to 700 g. per liter.

The potentials at both hydrogen and silver-chloride electrodes change during the process of inversion. The potential at the hydrogen electrode is also affected by a hydrogenation of sucrose or of the products of its inversion. The liquid-junction potential appears to be considerably changed by the addition of sucrose.

This last phenomenon, and to a smaller extent the second one, introduces a large uncertainty into the measurement of single-ion activities in these solutions, and therefore into the determination of the mechanism of the inversion process.

The values of the second cell are interpreted by theory, and some theoretical implications of the measurements with the first cell are discussed.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

A STUDY OF THE INFLUENCE OF THE ELECTRODES ON THE FORMATION OF OZONE AT LOW PRESSURES IN THE ELECTRICAL DISCHARGE

BY PHILIP T. NEWSOME[1]

RECEIVED MARCH 13, 1926 PUBLISHED AUGUST 5, 1926

The electrolysis of gases constitutes a field of investigation which is important because it connects ionization with chemical reaction. Lind[2] has pointed out that electrolysis in solution is a special case of electrolysis, and that it is simpler than the electrolysis of gases. In solution, all the chemical reaction occurs at the surface of the electrodes, and there is a simple relation between the number of molecules reacting and the number of electrons passing through the circuit. This relation finds expression in Faraday's law, which is one of the most exact laws in science.

In the case of gases, chemical reaction is brought about partly in the gas space between the electrodes by ions that combine before they can reach the electrodes. Under these conditions the number of electrons, *n*, recorded by the ammeter in the circuit is considerably less than the total number of ions, *N*, involved, and less than the number of molecules, *M*, reacting.

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[1] This communication is based on a thesis presented in 1926 at the University of Wisconsin for the degree of Doctor of Philosophy. The investigation was carried out under the direction of Farrington Daniels.

[2] Lind, *Trans. Am. Electrochem. Soc.*, **44**, 63 (1923).

Anderegg[3] observed an aging effect in ozonizers and drew the important conclusion that part, at least, of the ozonizing reaction occurs at the surface of the electrodes. The present investigation was undertaken with the idea of reducing the pressure of the gas and increasing the area of the electrodes so that most of the reaction would occur at the electrodes. It was reasoned that under these conditions the electrolysis might be similar to electrolysis in solutions, and that the ratio of the number of molecules reacting to the number of electrons registered in the circuit might have theoretical significance.

The electrical discharge in gases is so complicated that it was necessary to eliminate as many variables as possible. The composition of the gas was kept constant by a constant-flow method. Fluctuations in the discharge were eliminated by including a very high external resistance in the circuit. The geometrical arrangement of the electrodes was designed to give a minimum of field distortion, a large metallic cylinder being coaxial with a large wire. The wire was large enough to prevent the intense potential drop around a point, but small enough so that there was a pronounced difference in area between the two electrodes. This difference was necessary in drawing conclusions concerning the specific action of the electrode material. The input of energy was so low that there was no appreciable heating of the chamber. There was always a bead of light on the negative electrode, sometimes stationary and sometimes wandering, but since the results checked closely regardless of the position of the bead this was not considered to be a variable.

In this communication the results on ozone are reported. It was found that under the conditions of these experiments the electrodes played a fundamental part in the chemical actions, and that under certain conditions there seemed to be a relation between the number of electrons reaching the electrodes and the number of reacting molecules.

Description of Apparatus

The arrangement of the apparatus is shown in Fig. 1. The gas was stored over concentrated sulfuric acid in the large bottle at the left of the figure, and drawn through the system by a vacuum pump (not shown). By carefully adjusting the stopcock H it was possible to maintain any desired pressure in the discharge chamber, as measured by the manometer, M. The rate of flow under any conditions was measured by the flowmeter F. When it was necessary to measure the rate of flow of mixtures of ozone and oxygen, the flowmeter was kept at a specified level while the sample of the gas was passed through the side tube I and analyzed.

After passing through the discharge chamber, the ozone was absorbed in a solution of potassium iodide contained in a tall absorption bottle A.

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[3] Anderegg, *Trans. Am. Electrochem. Soc.*, **44**, 203 (1923).

All connections were of fused glass tubing except the connection K to the absorbing bottle, which was constructed with overlapping joints covered with wax. After an experiment, the solution was acidified with sulfuric acid and titrated with 0.0025 *N* sodium thiosulfate solution, using a starch indicator.

A constant current of two milliamperes was maintained through the discharge chamber by a set of radio dry batteries of 2200 volts connected through a variable resistance R and a calibrated galvanometer G. The resistance contained a screw adjustment whereby one could vary the distance between a fixed platinum disk and a mercury level in a 50–50 mixture of absolute ethyl alcohol and xylene.

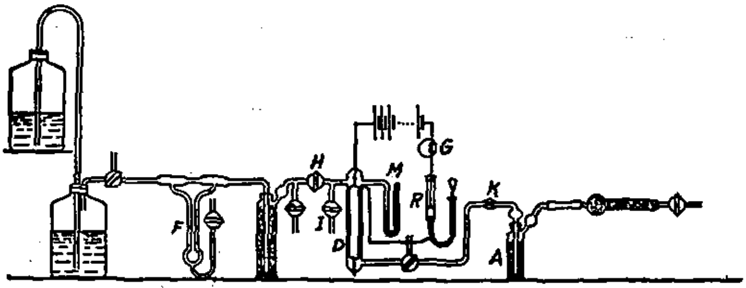

Fig. 1.—Apparatus for measuring the production of ozone at low pressures.

The vertical discharge chamber D consisted of a heavy copper cylinder 23.5 cm. long and 3 cm. inside diameter, slipped into a large glass tube. The tube was provided with inlet tubes and outlet tubes and a mercury manometer. Copper wire, 2.057 mm. in diameter, was strung through the center and set in position with de Khotinsky cement.

The silver and gold electrodes were made by electroplating the copper electrodes. The oxygen used in the experiments, taken from a commercial tank, was stored over sulfuric acid. The rate of flow of gas was about 27 cc. per minute, measured under 760 mm. pressure at 20°.

The inlet tube was above the copper cylinder and the bead of light stayed near the top of the cylinder. The incoming gas went downward through the bead of light and then came into contact with the large electrode area before passing out.

The relation between chemical action and ionization in these experiments is reported as M/n ratios, where M is the number of molecules reacting and n is the number of electrons reaching the electrodes. The number of electrons was determined by multiplying the amperes by the number of seconds to give coulombs, and dividing the coulombs by the charge of one electron (1.59×10^{-19} coulomb). The number of molecules was determined by converting the cubic centimeters of thiosulfate solution into moles of ozone and multiplying by the Avogadro number. Any M/n

ratio may be changed back to moles of ozone per coulomb by dividing by the factor 96,500.

It was gratifying to find that duplicate experiments checked closely. In most cases they agreed within the limit of the analytical accuracy and showed that the conditions of the discharge were completely reproducible. The average values, only, are given in the tables and the following examples, taken at random, are included to show the agreement in the *M/n* ratios: 0.21, 0.22, 0.21; 0.67, 0.67, 0.67; 2.73, 2.73, 2.75.

The Influence of Pressure on the Formation of Ozone

The pressure was varied from 14 mm. to 33 mm. Experiments could not be carried out below this range on account of the vapor pressure of the water in the absorbing solution, and above this range the discharge did not operate smoothly with the batteries which were available. The results of the experiments are summarized in Tables I and II and in the corresponding curves of Fig. 2.

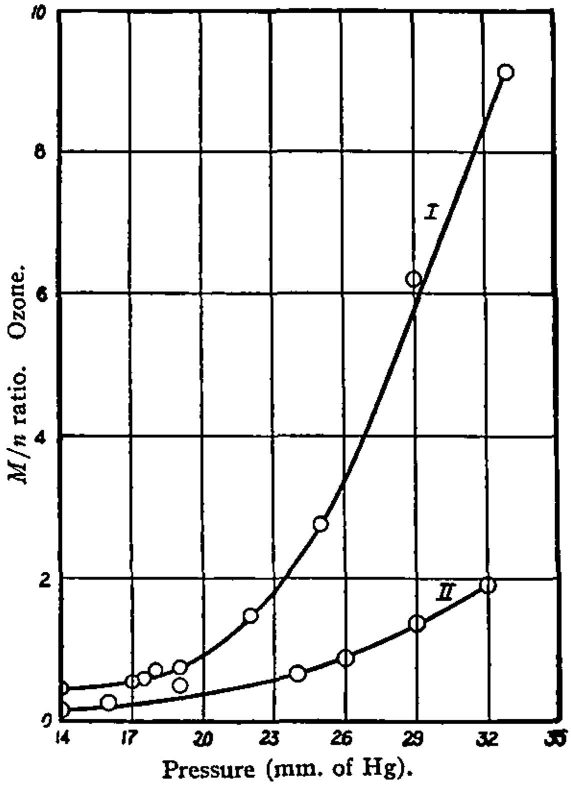

Fig. 2.—The influence of pressure on the *M/n* ratios. Cylinder negative. Upper curve—copper electrodes; Table I. Lower curve—gold electrodes; Table II.

As seen in the upper curve of Fig. 2, at low pressures the *M/n* ratio appears to approach a constant value of 0.5, which is the value corresponding to Faraday's law. This number suggests that two electrons are involved in the formation of ozone. In view of the later experiments, however, it is not certain that this ratio is significant.

In the case of gold electrodes a value considerably less than 0.5 is indicated for the *M/n* ratio at low pressures. The best explanation seems to be that gold catalyzes the decomposition of ozone. It is more effective in this decomposition when the electrode of larger area is charged positively, as shown by the last two results.

The greater production of ozone with the cylinder negative does not agree with the results of other investigators at atmosphreic pressure,

TABLE I

INFLUENCE OF PRESSURE. COPPER ELECTRODES

Time, min.	Current, milliamp.	Charge on cylinder	Pressure, mm.	Molecules of ozone formed per electron
5	2.19	−	33	9 14
5	2.15	−	29	6.20
10	2.03	−	26	3 53
5	2.19	−	25	2 75
10	2.15	−	22	1.48
10	2.15	−	19	0.75
15	2.15	−	18	.72
10	2.15	−	17.5	.59
10	2.15	−	17	.55
5	2.15	−	14	.46
		+	26	.25
		+	24	.14

TABLE II

INFLUENCE OF PRESSURE. GOLD ELECTRODES

10 minutes 2.19 milliamperes

Charge on cylinder	−	−	−	−	−	−	−	+	+
Pressure, mm.	32	29	26	24	19	16	14	24	23
M/n	1.91	1.38	0.881	0.670	0.513	0 258	0 153	0.365	0 305

shown in Table III, but it must be emphasized that the different conditions make a direct comparison impossible. Apparently no work has been done before on the electrolysis at low pressures. The influence of the electrodes is probably more important at the lower pressures.

TABLE III

RESULTS OF OTHER INVESTIGATORS AT ATMOSPHERIC PRESSURE

	Kunz and Rideal[4]		Warburg[5]		Anderegg[6]	
Charge on cylinder	+	−	+	−	+	−
M/n	90.54	48.29	86.52	34.20	36.35	30 00

The Aging of the Electrodes

It was soon found that the yield of ozone changed with time, a phenomenon discovered by Anderegg.[6] Table IV and Fig. 3 show that an increase in the duration of the experiment increased the efficiency of the production of ozone, when the cylinder was positive, but that time was not a variable when the cylinder was negative.

The upper curve, A, of Fig. 3 with the cylinder negative is a straight line, showing that the amount of ozone formed is directly proportional to the time, or to the input of electrical energy (current constant). The results are high indicating little, if any, de-ozonization. The lower curve,

[4] Kunz and Rideal, *J. Phys. Chem*, **24,** 379 (1920).

[5] Warburg, *Ann. Physik,* **13,** 464 (1904).

[6] Anderegg, THIS JOURNAL, **39,** 2581 (1917).

Table IV

Duration of Discharge. Copper Electrodes

A. Cylinder negative 26 mm. pressure; 2.03 milliamperes			B. Cylinder positive 26 mm. pressure; 2.33 milliamperes		
Time, min.	Ozone, millimoles	M/n'	Time, min.	Ozone millimoles	M/n'
5	0.0222	3.51			
10	.0446	3.53	10	0.00367	0.25
15	.0653	3.45	20	.0100	.34
20	.0898	3.56	30	.0276	.63

B, with the cylinder positive shows a considerably smaller yield of ozone, probably because the large positive cylinder decomposes the ozone, but as the discharge continues to pass, the decomposition becomes less and the yield of ozone, per *minute*, increases. This gives to the curve an increasing slope. The aging effect with the cylinder positive was only temporary. When the discharge was stopped and another experiment started within an hour, the M/n ratio was again low, and the data of Table IV could be repeated as often as desired. These facts suggest that the copper atoms of the positive electrode decompose ozone, but that the discharge causes them to become covered with a film of protecting material (possibly a higher oxide). The "poisoning" of the electrode surface tends to reach a maximum, and increased exposure gives less increase in the M/n ratio after the discharge has been operating for some time. The protecting material must be unstable, for the de-ozonizing effect quickly returns to its original value when the current is turned off.

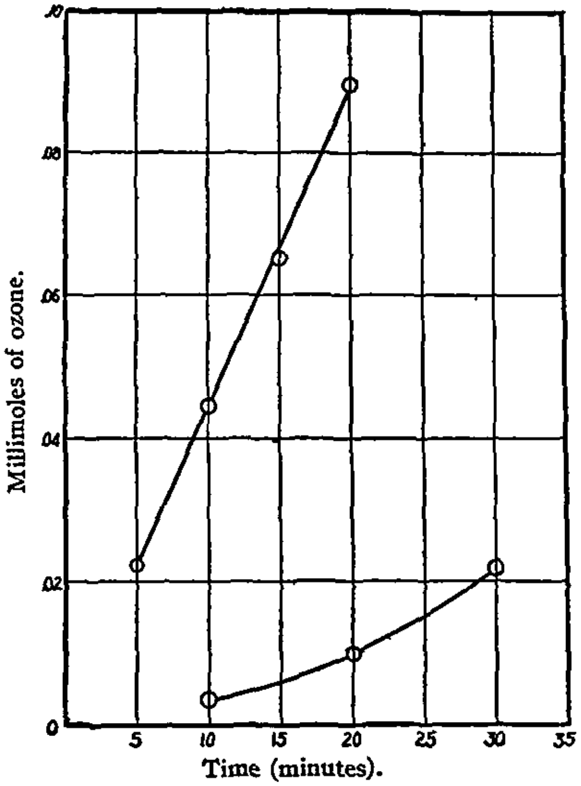

Fig. 3.—The influence of time of discharge on efficiency of ozone production. Copper electrodes. *A*. Upper curve—cylinder negative. *B*. Lower curve—cylinder positive.

A similar aging effect was observed with gold electrodes, and the M/n ratios increased with the duration of the discharge. In this case it was found that rinsing the electrodes with distilled water, caused the M/n ratio to fall to its original low value.

In order to study the influence of the electrodes from a different angle, the copper electrodes were given absolutely fresh surfaces by etching with nitric acid, and a series of five-minute exposures was made. The results are given in Table V.

TABLE V

FIVE-MINUTE EXPOSURES OF FRESHLY-ETCHED COPPER ELECTRODES

Cylinder negative; 26 mm. pressure; 2.15 milliamperes

Exposure no.	1	2	3	4	5	6	7
M/n	0.422	1.25	1.82	2.00	3.26	3.53	3.45

Apparently the new copper surface is active in decomposing ozone, even though it is charged negatively, but after being in the discharge a short time its efficiency is impaired and after 30 minutes it is rendered completely inactive. The M/n ratios increase (on account of a lessening of the de-ozonizing effect) until they reach a maximum value which agrees with the third experiment of Table I. The whole series was checked closely after etching a second time and repeating the experiment. After the copper surface became sufficiently aged to be inactive in decomposing ozone, when acting as the cathode, it was nevertheless active when made the positive electrode in the discharge, and the M/n ratios with the cylinder positive were again low as in the last experiments of Table I.

The Influence of the Electrode Material

Gold, silver and aluminum were used as well as copper, in studying the influence of the electrodes on ozone formation. By the use of mixed electrodes it was possible to gain additional information concerning the place where the ozone is formed and decomposed. The results are summarized in Table VI.

TABLE VI

INFLUENCE OF ELECTRODE MATERIAL

24 mm. pressure 1.9–2.2 milliamperes

Cylinder	Charge	Wire	Charge	M/n
Cu	+	Cu	−	0.14
Cu	−	Cu	+	2.35
Au	+	Au	−	0.36
Au	−	Au	+	.67
Au	+	Ag	−	.24
Au	−	Ag	+	.69
Ag	+	Ag	−	.13
Ag	−	Ag	+	.14
Ag	−	Cu	+	.21
Al	+	Al	−	.10
Al	−	Al	+	.10
Al	+	Cu	−	.10
Al	−	Cu	+	.09

These results may be interpreted on the hypothesis that the ozone produced is fairly constant, but is decomposed at the metallic surface of the electrodes. The area of the cylinder is so much greater than the area of the wire that the effect of the cylinder largely overshadows that of the wire. The catalytic de-ozonation is greater when the metal is charged positively. All the ozone yields are low except the one where the copper cylinder is negative, for in this case the copper cylinder appears to be inactive in decomposing ozone and the positive copper wire is small in area. The de-ozonizing effect seems to increase in the order copper, gold, silver, aluminum. The greater effect of the metal, when positively charged, is pronounced in the case of copper and gold, but it is not evident in the case of silver and aluminum because the decomposition is so great with these metals anyway, that any difference is minimized.

The Decomposition of Ozone

To test further, the hypothesis already proposed, the influence on ozone decomposition of electrode material and positive or negative charge was studied. Oxygen containing about 2% of ozone was passed through the discharge chamber under conditions similar to those already described. The results are summarized in Table VII.

TABLE VII

THE DECOMPOSITION OF OZONE

Current, 2.19 milliamperes; time, 10 minutes

Electrodes Cylinder	Wire	Charge on cylinder	Pressure mm.	O_3 entering, millimoles	O_3 leaving, millimoles	O_3 decomposed %
Au	Au	none	28	0.1685	0.1685	00.00
		–	28	.1428	.0278	80.5
		+	28	.1357	.0119	91.2
Au	Ag	none	27	.1155	.1104	4.4
		–	24	.0584	.00492	91.6
		+	24	.0584	.00275	95.3
Au	Cu	+	24	.0990	.00647	93.5
		+	24	.0702	.00468	93.3
Cu	Cu	none	24	.0960	.0948	1.2
		–	24	.1018	.00972	90.4
		+	24	.1018	.00965	90.5
Al	Al	none	21	.0646	.0642	0.3
		–	21	.0646	.0043	93.3
		+	21	.0646	.0042	93.5

An examination of the table shows that there is very little decomposition of ozone in passing through the chamber in the absence of the electrical discharge, except in the case of silver, and silver is known to be an excellent catalyst for the decomposition of ozone. When the discharge is passing, the decomposition is usually 90% or more complete. The decomposition is so great that the influence of the different factors is partly lost. It is evident, however, that the decomposition of ozone increases in the order copper, gold, silver, aluminum. The results with the gold cylinder support strongly the hypothesis that the decomposition of ozone is greater when the cylinder of larger area is charged positive.

The Voltage Factor

Although the potential drop across the chamber is not involved in the determination of M/n ratios, it is an important factor in ozone formation, particularly from the practical view of energy consumption. Good ozonizers working at atmospheric pressure yield about a gram molecule of ozone for a kilowatt hour input of electrical energy. Even this is a very low yield calculated on the thermochemical basis. It seemed worth while to determine the relation between ozone production and input of electrical *energy* under these new conditions of low pressure and chemically active electrodes.

The potential drop across the electrodes was determined with an electrostatic voltmeter. With copper electrodes the voltage, V, required to maintain a current of 2.19 milliamperes is given by the following equations in which P represents the pressure of oxygen in mm. of mercury: $V = 305 + 6P$ (cylinder —); $V = 265 + 6P$ (cylinder +). These equations are valid only for the particular discharge chamber used in these investigations and for the pressure range from 15 to 35 mm. The measurements were made with a constant stream of oxygen passing through, under the conditions of the previous experiments. The addition of 2% of ozone to the oxygen did not appreciably affect the voltage required to maintain the current and the voltage was constant within the limits of experimental measurement no matter how long the discharge was passing.

The yield of ozone in moles per kilowatt hour can readily be calculated from the M/n ratios by dividing by the faraday (96,500) and the voltage drop and multiplying by the number of joules in a kilowatt hour (3.6×10^6). With the copper cylinder charged negatively the highest values of M/n were obtained. Under these conditions at 24 mm. the efficiency was 0.2 mole of ozone per kilowatt hour. With the other electrode arrangements the yield was lower. At higher pressures the yields on the energy basis are greater.

Conclusions

The experimental results have been interpreted on the hypothesis that an important factor influencing the yield of ozone in these experiments is the de-ozonizing action of the electrodes, particularly the positive electrode. The mechanism of the destruction of ozone at the electrodes is not clear, but the experiments with aluminum electrodes are significant. It is known that aluminum is completely covered by a protecting film of oxide and that ozone is not decomposed by this coated aluminum. In fact, aluminum was used in the experiments because it was thought that with it there would be no de-ozonation at all. It was a surprise, then, to obtain the very low concentration of ozone, when the discharge was operating.

It seems likely that the bombardment of electrons on the positive aluminum electrode disintegrates the film of aluminum oxide and leaves free or partly free aluminum atoms at the surface, which then are immediately oxidized by the ozone (and by the oxygen) with the resulting destruction of the ozone. This hypothesis may also be applied to the other metals.

The conditions for the formation of ozone are more obscure. In the electrical discharge at these pressures the fall of potential is greatest near the negative electrode if the electrodes are of the same dimensions. The bead of light was always more intense at the negative electrode. These facts suggest that the ozone may be formed by electronic bombardment at or near the negative electrode. The present data do not enable one to decide whether the material of the electrodes influences the quantity of ozone actually synthesized, or whether it influences the final quantity only by decomposing part of the ozone that has already been formed.

It is a striking fact that under the conditions which give the highest yield of ozone, the M/n ratio, extrapolated to zero pressure, is practically 0.5 and corresponds to one molecule of ozone for every two electrons. Further experiments are necessary before it can be decided whether or not this ratio is significant. Certainly in the other cases, the de-ozonization process destroyed the theoretical significance of the M/n ratio, and it remains to be seen whether de-ozonation is still taking place to an appreciable extent when the copper cylinder is negative. It may be more than a coincidence that the ratio of the inside of the copper cylinder to the area of the wire is 14.5, and that the ozone production is fourteen times as great with the cylinder negative as with the cylinder positive. This ozone ratio of 14 to 1 was obtained only with copper electrodes, although the dimensions of the other electrodes were identically the same. In these cases, however, it is certain that some de-ozonization was taking place, even with the cylinder negative, for the M/n ratios are lower.

Experiments similar to those just described with ozone were carried out with ammonia. In both cases the gases passed through the chamber fairly rapidly and equilibrium conditions in the discharge were not reached. The thermal equilibrium in the two cases was different, that of ozone being a decomposition and that of ammonia being a synthesis. The catalytic effects of the electrodes were also different.

Each experiment lasted for 20 minutes, and the current was kept constant at 1.9 milliamperes and the gas velocity at 9 cc., per minute. The results are summarized in Table VIII.

Starting with hydrogen and nitrogen under the same conditions practically no ammonia was synthesized.

TABLE VIII

THE DECOMPOSITION OF AMMONIA

Wire	Cylinder	Pressure, mm.	Positive wire: NH_3 decomposed, %	Positive wire: M/n	Negative wire: NH_3 decomposed, %	Negative wire: M/n
Al	Al	25	3.1	11.0	1.9	6.6
Fe	Al	22	2.2	7.1	1.6	5.6
Cu	Cu	23	3.4	12.1	2.9	9.9

The author wishes to express his appreciation to Professor Farrington Daniels for the assistance and instruction given during the course of this research.

Summary

1. The production of ozone has been investigated at pressures from 14 mm. to 33 mm. under conditions designed to emphasize the action of the electrodes.
2. The quantity of ozone produced per coulomb of electricity passing through the circuit decreased with decreasing pressure and approached a constant value.
3. The production of ozone was largely influenced by the material of the electrode. The efficiency decreased in the order: copper, gold, silver, aluminum. Experiments were also carried out with mixed electrodes.
4. Under certain conditions the yield of ozone increased as the electrodes became aged in the electrical discharge.
5. The results are in accord with the hypothesis that part of the ozone formed in the discharge is decomposed at the positive electrode.
6. Calculated as moles of ozone per kilowatt hour the efficiency is rather low.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OHIO STATE UNIVERSITY]

A NEW TYPE OF END-POINT IN ELECTROMETRIC TITRATION AND ITS APPLICATION TO IODIMETRY

BY C. W. FOULK AND A. T. BAWDEN

RECEIVED MARCH 22, 1926 PUBLISHED AUGUST 5, 1926

The scheme of electrometric titration offered in this paper is a special case of the bimetallic electrode systems described by Willard and Fenwick[1] and discussed later by Van Name and Fenwick.[2] It was, however, not inspired by these investigations but was discovered accidentally by one of us in the preparation for the titration of iodine electrometrically in the conventional way. The suggestion thus offered by chance was then followed. The characteristic features of this scheme as finally worked out

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[1] Willard and Fenwick, THIS JOURNAL, **44**, 2504 (1922).

[2] Van Name and Fenwick, *ibid.*, **47**, 9, 19 (1925).

are the simplicity of the equipment required and the sensitiveness and peculiar character of the end-point.

Details of the Apparatus and Procedure

Fig. 1 illustrates the arrangement of the apparatus used. G is a suitable galvanometer. In our experiments two types were used, one a Leeds and Northrup box with enclosed lamp and scale, and one the needle instrument which is part of the Wendt titration apparatus. R is a Beck Brothers rheostat, 50 ohms and 3.3 amp.; B is an Edison cell; C is a beaker for the titrations and E, E are platinum wire electrodes. A motor-driven stirrer that was used is not shown. The essential feature of the procedure is the adjustment of the resistance so that the potential difference between the electrodes is only 10 to 15 millivolts.

When iodine, for example, is titrated by means of this simple apparatus with a thiosulfate solution it will be found that when nearly all of the iodine has been reduced the light spot of the galvanometer comes info view and, as successive drops of the thiosulfate solution are added, the spot approaches the zero of the scale until, coincident with the disappearance of the last trace of the iodine, it comes to rest at zero and remains there even when an excess of thiosulfate solution is added. When the reverse titration is made, that is, when iodine is added to thiosulfate, the nature of the end-point is reversed. During the early part of the titration the light spot of the galvanometer remains at zero but as the end of the reaction approaches, the spot makes temporary excursions returning, however, to its zero position as stirring proceeds. Finally, the end-point is indicated by a permanent displacement which is increased by further additions of iodine from the buret.

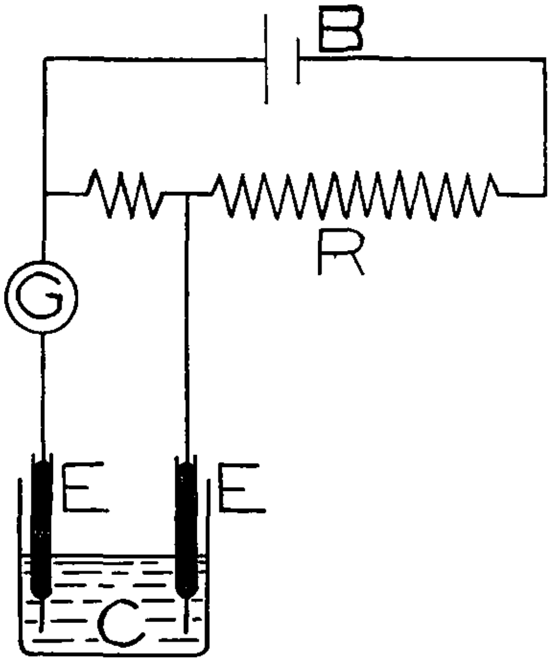

Fig. 1.—Apparatus.

Since this type of end-point is characterized by the galvanometer coming to a dead stop or by its permanent displacement from a position of rest, the name "dead-stop" end-point is suggested.[3]

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[3] "Polarization" end-point would perhaps be a better name but it was not used because of probable confusion with other polarization applications in electrometric titrations; such, for example, as the work of Willard and Fenwick.

Theory of the Dead-Stop End-Point

Willard and Fenwick[4] and later Van Name and Fenwick[2] have shown that metallic electrodes of the type used here owe their effect in electrometric titrations to gas reactions taking place on the surface and have discussed in so exhaustive a manner the theory of the behavior of such electrodes that nothing need be added here excepting the details applying to the dead-stop end-point. By way of variety, however, and because we are concerned only with the practical application of this phenomenon to titrations, we shall depart from the conventional method of using mathematical equations to show the potential changes that occur at and near the end-point and shall discuss the situation in a purely qualitative way. Our point of view will at least be found adequate for predicting new applications.

The fundamental condition for the production of the dead-stop end-point is the use of so low a potential (10 to 15 millivolts) between the electrodes in the solution to be titrated that the back electromotive force of polarization[5] balances it and consequently no current flows, the galvanometer registering zero.[6] Under these conditions the dead-stop end-point will occur in the titration of all systems in which a sharp transition from the polarization of at least one electrode to the complete depolarization of both of them (or *vice versa*) coincides with the end of the reaction. We assume that polarization is due to oxygen adsorbed on the anode and hydrogen on the cathode and that the anode can, therefore, be depolarized by a suitable reducing agent and the cathode by a suitable oxidizing agent.

It is obvious that from the standpoint of the condition of the electrodes during a titration only three cases can exist. (1) One electrode only is polarized. The titrating solution from the buret must then depolarize this electrode. This is the situation in the titration of thiosulfate or of arsenite with iodine. The anode remains depolarized throughout the titration due to the reducing agents present and at the end-point the first trace of iodine in excess depolarizes the cathode. (2) Both electrodes remain depolarized. This presupposes the presence in the solution of both an oxidizing and a reducing agent which do not react with each other, or at any rate, not in an irreversible way. It is the situation in the titration of iodine with thiosulfate or arsenite. (3) Both electrodes are polarized. The titrating solution must then be capable of depolarizing them both.

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[4] Ref. 1, p. 2516.

[5] The first suggestion that simple polarization was the probable explanation of the dead-stop end-point came to us from Dr. W. G. France.

[6] The zero position of the galvanometer is not absolutely essential. It was found as a matter of practice that if the needle or light spot stood close to zero, this position would serve as the point of reference for this type of end-point. There was, however, no advantage in this.

This is possible because mixtures of reagents may be used as titrating solutions but, as a rule, Case 3 could be transformed into Case 1 by the addition of a suitable reagent.

In general, at least one of the main constituents of the reaction must be an efficient depolarizer and the products of the reaction must not act as depolarizers and thus vitiate the end-point. In iodimetric titrations, for example, the sodium tetrathionate and the sodium arsenate which form are not cathodic depolarizers. As in other titrations, the sharpness of the end-point is proportional to the degree of irreversibility of the reaction.

Finally, it should be pointed out that the necessary polarizing or depolarizing conditions are not limited to those directly produced by the constituents of the main reaction. They can be brought about indirectly by the action of one of these main constituents upon a suitable added substance or mixture of substances. For example, a sharp dead-stop end-point can be obtained on titrating a strong base with a strong acid if there is present in the solution of the base a small amount of iodide and a suitable oxidizing agent. This interesting application of electrometric titration to neutralization reactions is now being studied in the Ohio Laboratory.

Experimental Evidence on the Above Points

With the electrodes in a solution of potassium chloride no current flowed when iodine was added because the anode remained polarized. The addition of a little iodide at once caused a deflection of the galvanometer. In another experiment the iodide was added first but without effect. The electrodes were then tried in separate vessels containing iodide solutions of the same strength connected by a salt bridge. No current flowed unless a trace of iodine was present in the cathode vessel. If this electrode, though bathed in iodine, was made the anode, the current ceased.

Characteristics of the Dead-Stop End-Point

The dead-stop end-point possesses the three most desirable characteristics of an end-point. (1) It gives evidence of its approach by the behavior of the galvanometer. (2) If overrun the fact is at once apparent. (3) It is very sensitive. (The behavior of the galvanometer at and near the end-point and the effect of overrunning the end-point are described in an early paragraph above.) Finally, equilibrium is reached almost instantly, so that there is no tedious waiting in the neighborhood of the end-point.

The sensitiveness or response of the dead-stop end-point to slight changes in concentration of the main constituents of the reaction is remarkable. Under favorable conditions in the titrations of iodimetry two or three drops, more or less, of 0.001 N solution are sufficient to give an end-point. Under ordinary conditions, however, a drop of 0.01 N to 0.005 N solution is required. Colored substances, solids in suspension and various organic liquids have no effect unless, of course, there is direct reaction.

Application to Iodimetry

Titrations of iodine with either sodium thiosulfate or sodium arsenite and titrations of these two substances with iodine can be made with the apparatus shown in Fig. 1. A potential of 10 to 15 millivolts[7] between the electrodes should be used and a motor-driven stirrer must, of course, be provided.

The chemical conditions for the titrations should be the same as those used with starch as indicator. It will be found, however, that the dead-stop end-point is less affected by variations in conditions than is the starch blue. For example, the concentration of potassium iodide, sodium hydrogen carbonate and acid may vary within wide limits. Titrations can also be made in strong alcohol or glycerol solutions if 2% potassium iodide is present. Temperatures approaching 100° also have no effect.

The character and sensitiveness of the dead-stop end-point in iodimetry have been described above. It is perhaps more sensitive with arsenite solutions than with thiosulfate. The relation to the starch end-point is interesting, being the equivalent of about 4 drops of 0.001 N solution removed, in the sense that in titrating with iodine the electrometric end-point occurs before the starch blue appears and, conversely, in titrating iodine with thiosulfate or arsenite it occurs after the blue has disappeared. In other words the depolarization of the cathode under the conditions of the titration is a much more sensitive test for iodine than the reaction with starch. This also answers the question that should be raised about a new volumetric process, namely, what is its end-point error, or the amount of titrating substance required to produce the end-point? In this case it is easily seen that the excess of iodine to give the dead-stop end-point is negligible, less than the concentration needed for the starch end-point.

The reproducibility of the dead-stop end-point was tested by titrating a series of 25.00cc. portions of 0.001 N iodine solution in 2% potassium iodide solution (measured at the end of the titration) with approximately 0.002 N sodium arsenite solution. Twelve successive titrations were made, the average volume of arsenite required being 13.31 cc. The greatest deviation from this average was 0.06 cc. In another experiment five portions of from 25 to 33 g. of 0.1 N iodine solution were titrated with a somewhat more concentrated thiosulfate solution. Weighing burets were employed, the end-point being obtained in each case by the use of small amounts of 0.001 N solution. On calculating these five results to the common basis of 25.00 g. of iodine solution, the corresponding weights of thiosulfate were found to be 23.51, 23.52, 23.52, 23.52 and 23.53 g. These titrations were made with a Wendt apparatus which employs a needle galvanometer.

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[7] It is not necessary to use an instrument for measuring the potential. Adjustment of the resistance so that the galvanometer is just brought to zero with at least one electrode polarized is sufficient.

Another question that may be raised concerns reactions around the anode. Theoretically, the depolarization of this electrode with iodide should result in some free iodine and, indeed, after long standing a faint test for iodine can be obtained. During the period of a titration, however, such liberation of iodine at the anode is undetectable.

Electrometric Titration without a Battery

The following experiment is perhaps only a bit of chemical by-play, but it is presented because of its interest and because it may suggest some practical application.

If two vessels, one containing dilute and the other concd. potassium iodide solution, are connected by a salt bridge and a metallic circuit through a galvanometer as shown in Fig. 2, the vessel containing the weaker solution can be used for the titrations of iodimetry by the dead-stop end-point method because the concentration chain formed by the two iodide solutions gives a sufficient potential for the purpose. The anode in the stronger solution remains permanently depolarized and the cathode in the weaker solution is polarized in the presence of an excess of thiosulfate or arsenite and depolarized if iodine is present. Many titrations were made with this arrangement which may be considered the simplest that has yet been used in electrometric work.

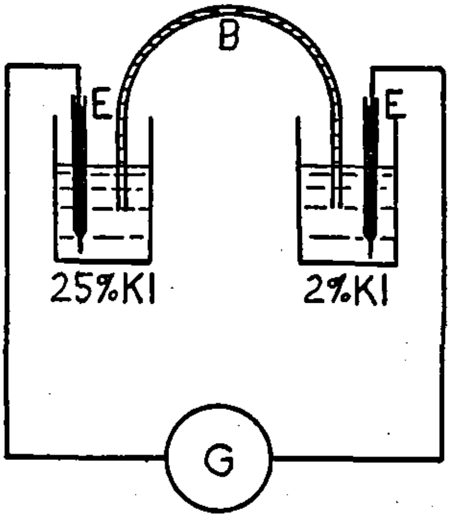

Fig. 2.—Concentration chain for titrating without a battery.

Other Applications

The dead-stop end-point scheme has been successfully applied to oxalate-permanganate titrations. It was also found, incidentally, that a very sharp end-point can be obtained in the direct titration of thiosulfate with permanganate and *vice versa.*

Summary

This paper contains the description and theory of a simple bimetallic electrode system for electrometric titrations, the fundamental principle of which is the use of a potential between the electrodes of the same order of magnitude as the counter electromotive force of polarization.

There is included a description of a novel arrangement which depends upon a concentration chain, composed of two potassium iodide solutions connected by a salt bridge, for the necessary impressed potential between

the electrodes. Iodimetric titrations can be made in the weaker of the two solutions without the use of a battery.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE CRYOGENIC LABORATORY, BUREAU OF MINES, UNITED STATES DEPARTMENT OF COMMERCE]

THE VAPOR PRESSURE OF ETHANE NEAR THE NORMAL BOILING POINT[1]

BY A. G. LOOMIS AND J. E. WALTERS

RECEIVED MARCH 29, 1926 PUBLISHED AUGUST 5, 1926

Introduction

For the design of an efficient plant to extract helium from natural gas it is necessary to know the thermodynamic properties of the several components of the gas. This investigation supplies the vapor pressure of ethane in the neighborhood of the normal boiling point, and is one of a series of investigations now being undertaken on the thermodynamic properties of the pure components of natural gas, and of their binary mixtures. The pressures recorded in this paper cover the range from 0.0245 atmospheres to 2.1441 atmospheres; Dr. Porter (see the following paper) has extended these measurements to the critical pressure.

Previous Investigations

Olszewski[2] reports the normal boiling point of ethane prepared from zinc ethyl as —93°.

Burrell and Robertson[3] measured the vapor pressure from 1 mm. to 760 mm., giving 183.8°K. as the normal boiling point. Temperatures were measured by means of a pentane thermometer, and two observers could check readings to 0.2° and in most cases to 0.1°. The cryostat of the Henning type could be held constant to 0.04° for the period of measurement of a vapor pressure. Pressure readings were reproducible to 1 mm. The limit of accuracy of reading the thermometers (0.2°) corresponds to 7.5 mm. near the normal boiling point. The ethane used was prepared from sodium acetate solution by electrolysis, purified chemically, fractionated and pumped free from traces of foreign gases. Moreover, portions were removed from time to time, so that the purity of their ethane was all that could be desired.

Maass and McIntosh[4] measured the vapor pressure from 288 mm. to 765 mm. and found 184.6°K. as the normal boiling point. Temperatures were read on a hydrogen gas thermometer; the cryostat could be held con-

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[1] Published with the permission of the Director of the Bureau of Mines.

[2] Olszewski, *Berl. Ber.*, 27, 3305 (1894).

[3] Burrell and Robertson, THIS JOURNAL, 37, 1893 (1915).

[4] Maass and McIntosh, *ibid.*, 36, 737 (1914).

stant to 0.1°. Their ethane was prepared from methyl iodide by means of a zinc-copper couple, chemically purified, cooled in spirals at —78°, and the middle fraction of several distillations accepted as pure. However, it has been shown by Kuenen[5] that ethane prepared from methyl iodide by means of a zinc-copper couple contains a heavier constituent, presumably butane, and since the latter has an appreciable vapor pressure at —78° a limited number of fractionations at this temperature would not remove all of it from the ethane, a circumstance which may explain their somewhat high value of 184.6°K. for the normal boiling point of ethane.

Experimental Part

Preparation of Ethane.—Ethane was prepared by the electrolysis of potassium acetate solution, following the methods of Murray.[6] The impure ethane was repeatedly circulated between two reservoirs of potassium hydroxide solution and allowed to remain in contact with this solution for several days. It was then allowed to bubble at a slow rate through fuming sulfuric acid to remove unsaturated gases, through sulfuric acid, and finally through potassium hydroxide solution; this procedure was repeated a number of times. The gas was finally dried over solid potassium hydroxide and phosphorus pentoxide, and frozen with liquid air. The solid ethane was pumped free from uncondensed gases by means of a mercury diffusion pump, the ethane then distilled to another bulb and pumped again, this procedure being repeated until no more gas was given off. The ethane was then repeatedly fractionated while being stirred with a small magnetic stirrer, only the middle portions being retained, and finally condensed into the vapor-pressure bulb. The temperature of the cryostat was adjusted so that the pressure was about one atmosphere, and it was found that repeated removals of small fractions of the sample did not change the pressure reading, proving that the ethane was pure.

Ethane prepared by the action of water on ethylmagnesium iodide and purified in the same manner as described above showed the same vapor pressure as ethane prepared by the first method.

Auxiliary Apparatus.—The cryostat employed was that described by Walters and Loomis,[7] and the temperature was maintained constant to 0.01° during the period of measurement.

For measurement of temperature we used platinum-resistance thermometer No. 2, made and calibrated as described by Loomis and Walters.[8] The temperature scale was defined by the Henning equation based on the calibration points; the observed and calculated temperature of the carbon dioxide point checked to 0.01°.

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[5] Kuenen, *Proc. Roy. Soc. Edinburgh*, **21**, 433 (1897).

[6] Murray, *J. Chem. Soc.*, **61**, 10 (1892).

[7] Walters and Loomis, THIS JOURNAL, **47**, 2302 (1925).

[8] Loomis and Walters, *ibid.*, **47**, 2851 (1925).

The bridge was of the Mueller type and had been calibrated by the Bureau of Standards.

Pressures were read on a manometer of wide inside bore by means of a Geneva Society cathetometer, calibrated by the Bureau of Standards; the cathetometer read directly to 0.001 cm. A Geneva Society standard meter was suspended near the mercury column for comparison on the cathetometer. At any particular temperature a series of readings was obtained, the temperature of the cryostat being temporarily varied so that the equilibrium pressure was approached from both sides. The containing bulb was shaken repeatedly to hasten the attainment of equilibrium. All pressures are expressed in terms of the normal atmosphere.[9]

Results

In Table I are given the results, each pressure being the mean of at least four readings with rising and falling meniscus. The data are well represented by the following equation; $\log_{10} P_{(\text{atm.})} = -(780.24/T) + 4.2563 - 0.000103T - 9.3 \times 10^{-10}(T - 238)^4$. From the equation the normal boiling point of ethane is found to be 184.467°K.

TABLE I

VAPOR PRESSURE OF ETHANE

T,°K.	$P_{\text{atm.}}$ (calcd.)	$P_{\text{atm.}}$ (obs.)	P(obs.) − P(calcd.)
167.836	0.3695	0.3693	−0.0002
165.529	.3162	.3160	− .0002
162.629	.2582	.2573	− .0009
158.385	.1890	.1886	− .0004
154.546	.1402	.1400	− .0002
147.324	.0762	.0759	− .0003
143.267	.0526	.0522	− .0004
135.736	.0247	.0245	− .0002
169.175	.4036	.4033	− .0003
171.700	.4747	.4743	− .0004
170.602	.4427	.4430	+ .0003
174.062	.5499	.5498	− .0001
175.708	.6076	.6073	− .0003
177.623	.6807	.6804	− .0003
178.621	.7215	.7210	− .0005
179.750	.7698	.7696	− .0002
181.506	.8500	.8499	− .0001
182.463	.8964	.8963	− .0001
183.778	.9633	.9634	+ .0001
184.539	1.0038	1.0040	+ .0002
185.137	1.0365	1.0366	+ .0001
185.914	1.0803	1.0800	− .0003
186.609	1.1206	1.1208	+ .0002
187.302	1.1620	1.1619	− .0001

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[9] The acceleration of gravity at the place of measurement was taken as 980.111 cm. sec.$^{-2}$.

TABLE I (*Concluded*)

$T, °K.$	$P_{atm.}$ (calcd.)	$P_{atm.}$ (obs.)	P(obs.) − P(calcd.)
187.72_6	1.1878	1.1881	+ .0003
188.37_9	1.2286	1.2289	+ .0003
189.11_4	1.2757	1.2761	+ .0004
189.85_8	1.3248	1.3264	+ .0016
190.79_1	1.3885	1.3900	+ .0015
191.43_0	1.4334	1.4347	+ .0013
192.28_6	1.4953	1.4974	+ .0021
192.77_7	1.5318	1.5340	+ .0022
199.90_9	2.1417	2.1441	+ .0024
196.24_4	1.8088	1.8110	+ .0022

The latent heat of vaporization of ethane at the normal boiling point is calculated to be 3642.4 cal. per mole from the thermodynamic equation $(\partial \ln P/\partial T)_p = \Delta H/RT^2$, using the equation given above to express P as a function of T. This value for ΔH is, of course, somewhat high resulting from the assumption of the perfect gas law in the thermodynamic equation.[10]

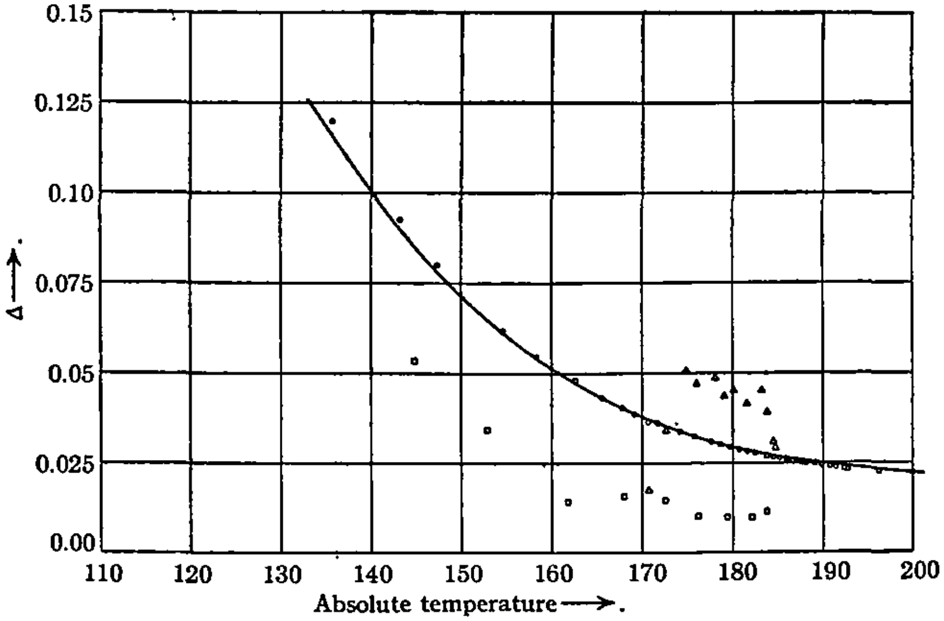

Fig. 1.—ΔT plot. Curve calculated from log P_{atm} = —$0.000103T - 9.3 \times 10^{-10} (T - 238)^4$. ○—Loomis and Walters. △—Maass and McIntosh. □—Burrell and Robertson.

For a comparison of the data of the several observers a plot is given representing the deviation Δ as a function of T, where Δ is log $P_{obs.}$ − log $P_{calcd.}$, the values of log $P_{calcd.}$ being obtained from the equation log $P_{calcd.}$ = —$(780.24/T) + 4.2563$, the first three terms of our equation representing

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[10] See the paper by Porter and Perry for the calculated value of ΔH based on specific volumes experimentally determined. THIS JOURNAL, 48, 2059 (1926).

the data. It is seen that our observations fall on a smooth curve lying between the somewhat scattered data of Maass and McIntosh and of Burrell and Robertson. The two remaining terms of the equation $[-0.00010\ T - 9.3 \times 10^{-10}(T - 238)^4]$ are calculated for several values of T and, as shown on the plot, fit the curve very closely.

Summary

The vapor pressure of pure ethane has been measured from a pressure of 0.0245 to 2.1441 atmospheres.

The equation derived from the data representing P as a function of T is $\log_{10} P_{\text{atm.}} = -(780.24/T) + 4.2563 - 0.000103T - 9.3 \times 10^{-10}(T - 238)^4$. The normal boiling point is calculated to be 184.467°K. from this equation.

A deviation plot is given which compares the data of the several observers.

The latent heat of vaporization at the normal boiling point of ethane is calculated to be 3642.4 calories per mole.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CRYOGENIC LABORATORY, BUREAU OF MINES, UNITED STATES DEPARTMENT OF COMMERCE]

THE VAPOR PRESSURES AND SPECIFIC VOLUMES OF THE SATURATED VAPOR OF ETHANE[1]

BY FRANK PORTER

RECEIVED MARCH 29, 1926 PUBLISHED AUGUST 5, 1926

The present work represents a part of a series of investigations that are being carried out on the properties of this substance. Measurements on the vapor pressure of ethane have been made by Hainlen,[2] Kuenen and Robson,[3] Maass and McIntosh,[4] Burrell and Robertson,[5] and Loomis and Walters.[6] Of these, only Kuenen and Hainlen extended their work to the higher pressures. The character of Hainlen's work does not conform to the present-day standards along this line. Kuenen did not succeed in getting his ethane completely pure, the variation in pressure at a constant temperature being as much as 1%.

Specific volumes of the saturated vapor have been measured only by Kuenen.[7] Only a short range below the critical was covered by this work.

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[1] Published with the permission of the Director of the Bureau of Mines.

[2] Hainlen, *Ann.*, **282**, 229 (1894).

[3] Kuenen and Robson, *Phil. Mag.*, [6] **3**, 149 (1902).

[4] Maass and McIntosh, THIS JOURNAL, **36**, 737 (1914).

[5] Burrell and Robertson, *ibid.*, **37**, 1893 (1915).

[6] Loomis and Walters, *ibid.*, **48**, 2051 (1926).

[7] Kuenen, *Phil. Mag.*, **40**, 173 (1895).

More accurate and complete data were considered desirable, especially for the calculation of the heats of vaporization over this range.

Ethane was generated by the electrolysis of a 60% solution of potassium acetate. It was allowed to stand over a solution of sodium hydroxide for some time and was then bubbled slowly several times through a train in which it successively passed through fuming sulfuric acid, ordinary concd. sulfuric acid, potassium hydroxide solution and phosphorus pentoxide. About 20 liters so treated was freed from air by freezing down with liquid air and evacuating several times, and then fractionated in a bead column of the Hempel type, the top of the column being refrigerated by a bath cooled to about —100°. Only a very small fraction of the ethane vaporized was removed, the remainder being refluxed down the column. About 3 liters of vapor from the middle portion was collected for the measurements. It was found to liquefy completely at a constant pressure within the limit of our measurements described below.

Temperature measurements were made with a platinum resistance thermometer, the calibration of which is described by Loomis and Walters.[8] The cryostat employed was also of the same type as used by those investigators.[9]

The pressure gage was of the type that was described by Keyes and Brownlee.[10] It had previously been calibrated against a mercury column of about 8 meters.

The dilatometer was made of heavy-walled Pyrex tubing, and had a volume of nearly 20 cc. A small capillary tube led from the lower end of the dilatometer up over the side of the cryostat and thence to the pressure gage. A small T connected this line through a steel valve to the volumenometer.

The volumenometer was a straight tube about 1 meter long with a total volume of 100 cc.

The dilatometer and volumenometer were calibrated in place. The heights of the mercury above reference marks were read with a cathetometer and the volumes of mercury removed were related to the readings on the cathetometer scale.

The filling of the dilatometer was accomplished by cooling it below the boiling point of ethane and allowing a suitable measured volume to flow in from the volumenometer.

The temperature of the volumenometer was kept very close to 25° and the pressure at one atmosphere. In order to arrive at the density of ethane under these conditions, for the purpose of determining the mass of ethane employed, an experimental method was used. The expansion

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[8] Loomis and Walters, This Journal, 47, 2851 (1925).

[9] Walters and Loomis, *ibid.*, 47, 2302 (1925).

[10] Keyes and Brownlee, *ibid.*, 40, 25 (1918).

on raising a certain volume from 0° to 25° was measured. The accepted density at 0° and 1 normal atmosphere is 0.0013562 g. per cc., and from this and our measurements the density at 25° and 1 normal atmosphere was found to be 0.0012383.

The exact volume of ethane vapor at a point of saturation was determined by holding the temperature constant and measuring the volumes and pressures at a series of points not far removed from the saturation point. By plotting these values on a large scale, the intersection of the curve with the vapor-pressure line could be readily ascertained and the volume of this point was taken as the saturated volume. The manipulation to obtain the part of the isotherm needed was comparatively simple. Starting with a small amount of liquid in the dilatometer, the vapor pressure was read. Then weights equivalent to about 0.001 atmosphere were removed from the pan of the gage and the mercury injector was backed up slowly until the gage was again in equilibrium with the pressure in the dilatometer. The volume occupied by the ethane in the dilatometer was then read and the process repeated until a sufficient number of observations were obtained to establish the curve.

The data of Latimer and Buffington[11] were used to correct for the thermal expansion of the Pyrex dilatometer. In calculating expansion due to pressure the Young's modulus of 0.6230 kg./sq. mm. was used. For temperatures below the freezing point of mercury, the mercury was kept at a position just above the level of the cryostat, and while the volume of the ethane was thus kept constant, the temperature and pressure were varied, with the vapor just above the condition of saturation. The isochor was then plotted and the break observed as before. The manipulation is not nearly so simple, because it is not so easy to change the temperature as it was to change the volume in the previous case.

The volume at the boiling point was obtained by connecting the dilatometer through the small capillary to the volumenometer and obtaining the isotherm near the saturation point.

The vapor pressures were found to be fairly well represented by the equation, $\log_{10} P_{\text{atm.}} = -780.24/T + 4.2563 - 0.000103T + 1.4 \times 10^{-11}(T - 238)^5$, in which the pressure is expressed in normal atmospheres. This equation, when applied at low temperatures, fits very approximately but not exactly to the data of Loomis and Walters.[6]

Table I gives the data obtained. The heats of vaporization given in Col. 5 are calculated from the exact thermodynamic equation, $dP/dT = \Delta H/T(V - v)$, where P is vapor pressure, T the temperature, ΔH the heat of vaporization, V the saturated vapor and v the volume of the liquid. The data of Maass and McIntosh[4] and of Kuenen[7] for the liquid densities were plotted and the values needed were read from the

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[11] Unpublished work from University of California.

smoothed curve. The values for dP/dT were obtained from differentiation of the above vapor-pressure equation, with the exception of that at the boiling point, which was obtained by differentiating the equation of Loomis and Walters.[6]

TABLE I

VAPOR PRESSURE OF ETHANE

T, °K.	$P_{atm.}$	$P_{obs} - P_{calcd.}$ atm.	V, cc./mole	ΔH, 15° calories per mole
288.26	33.468	+0.011	414.68	1739
283.58	30.106	+ .009	479.33	1890
278.84	26.837	− .073	552.23	2019
273.09	23.544	+ .003	649.24	2166
268.73	21.185	+ .023	736.84	2277
263.28	18.448	+ .009	861.23	2400
258.80	16.421	+ .020	968.6	2469
253.03	14.043	+ .026	1158.1	2624
248.65	12.354	− .027	1320.7	2692
243.22	10.536	− .014	1555.7	2789
238.90	9.229	− .013	1771.9	2849
234.58	8.044	− .010	2026.2	2907
226.18	6.073	.000	2652.2	3005
225.10	5.838	− .008	...	..
221.88	5.207	− .004	...	..
216.31	4.225	− .011	...	..
210.96	3.414	+ .011	...	..
205.62	2.733	+ .003	...	..
203.49	2.496	+ .005	...	..
184.47	0.9994	+ .005	14511	3325

An equation to represent the volumes was not found. Dieterici's equation of state was found to be the best simple equation of state to represent the values approximately. Using the data of Kuenen at the critical point to evaluate the constants, the calculated values were found to have a maximum deviation of 2.5% from observed values, with an average deviation of 1.3%.

Summary

The vapor pressures and specific volumes of the saturated vapor of ethane have been measured over the range from the normal boiling point to 288°K.

The data were used in the calculation of the heats of vaporization.

WASHINGTON, D. C.

[Contribution from the Cryogenic Laboratory, Bureau of Mines, United States Department of Commerce]

HIGH VAPOR PRESSURES OF NITROGEN[1]

By Frank Porter and J. H. Perry

Received March 29, 1926 Published August 5, 1926

The vapor pressures of nitrogen up to about one atmosphere have been measured by Wroblewski,[2] Baly,[3] Fisher and Alt,[4] Holst and Hamburger,[5] Cath[6] and von Siemens.[7] The data of von Siemens when corrected to the Leiden scale by Holst[8] agreed very well with those of Cath.

The higher vapor pressures have been measured by Olzewski[9] and Crommelin.[10] Olzewski used atmospheric nitrogen and the work was of a low accuracy. Crommelin's work was open to question for several reasons. He used boiling liquids as a cryostat without protecting the stem of the vapor-pressure bulb where it passes through the surface of the liquid. Unless the stirring is extremely vigorous, experience has shown that the bath may be considerably colder at the surface and the pressure correspondingly low. Furthermore, at the point 1.4727 atmospheres reported by Cormmelin, the temperature given is almost half a degree from the results obtained by Cath and von Siemens.

While Crommelin later states that this point is considerably less accurate than the others, the circumstance shows that there was probably some factor such as that already mentioned which disturbed the accuracy of the measurements. The measurement of the vapor pressure of nitrogen over this range, therefore, was considered to be worth while.

Apparatus and Material

The platinum-resistance thermometer and the cryostat used have already been described in reports from this Laboratory.[11,12] It was found convenient to use methane condensed from natural gas as a bath liquid for the lower temperatures. The pressures were measured with a deadweight gage of the type used by Keyes.[13]

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[1] Published with the permission of the Director of the Bureau of Mines.

[2] Wroblewski, *Wied. Ann.*, **25**, 371 (1885).

[3] Baly, *Phil. Mag.*, [5] **49**, 517 (1900).

[4] Fisher and Alt, *Ann. Physik*, **9**, 1149 (1902).

[5] Holst and Hamburger, *Z. physik. Chem.*, **91**, 513 (1916).

[6] Cath, *Verslag Akad. Wetenschappen Amsterdam*, **27**, 553 (1918).

[7] von Siemens, *Ann. Physik*, **42**, 871 (1913).

[8] Holst, *Proc. Akad. Wetenschappen Amsterdam*, **18**, 839 (1916).

[9] Olzewski, *Compt. rend.*, **99**, 133 (1884).

[10] Crommelin, *Verslag Akad. Wetenschappen Amsterdam*, **23**, 991 (1914).

[11] Walters and Loomis, This Journal, **47**, 2302 (1925).

[12] Loomis and Walters, *ibid.*, **47**, 2851 (1925).

[13] Keyes and Brownlee, *ibid.*, **40**, 25 (1918).

The nitrogen was generated from ammonium hydroxide and bromine water.[14] It was purified by standing over sodium hydroxide solution, passing through a trap cooled with liquid air, then over phosphorus and finally over phosphorus pentoxide. Three different samples were used, generated at different times. The third sample was further purified by a fractional distillation, but the vapor pressures agree very satisfactorily with the first two samples, showing that this method gives very pure nitrogen.

Table I gives the results, which are found to be fairly well represented by the equation $\log_{10} P = -302.34/T + 3.94127 - 0.000274T + 1.116 \times 10^{-6} (T - 100.5)^3$, in which the pressure is expressed in normal atmospheres. When extrapolated to low pressures this equation agrees fairly well with the data of von Siemens.

TABLE I

VAPOR PRESSURES OF NITROGEN

Temp., °K.	90.12	92.73	95.44	96.00	98.64	104.46	106.97	108.76	113.60	116.18	118.94	121.47
$P_{\text{obs.}}$, atm.	3.631	4.520	5.583	5.820	7.056	10.440	12.193	13.594	17.85	20.47	23.57	26 75
$P_{\text{obs.}} - P_{\text{calcd.}}$	—0.003	—0.003	0.000	—0.005	—0.006	—0.007	—0.009	0.035	—0.05	0.00	—0.06	—0.05

Summary

The vapor pressure of nitrogen has been determined in the range from 90.12°K. (3.631 atm.) to 121.47°K. (26.75 atm.). The results are represented fairly well by the equation $\log_{10} P = -302.34/T + 3.94127 - 0.00274T + 1.116 \times 10^{-6} (T - 100.5)^3$.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE CATALYTIC OXIDATION OF CARBON MONOXIDE

III. CATALYTIC EFFICIENCY OF MIXTURES OF DRY MANGANESE DIOXIDE AND CUPRIC OXIDE

BY WILLIAM C. BRAY AND GERALD J. DOSS

RECEIVED MARCH 31, 1926 PUBLISHED AUGUST 5, 1926

The mixtures of manganese dioxide and copper oxide considered in the first papers of this series[1] were prepared by kneading together measured quantities of the wet hydrated oxides. A "related series of catalysts" consisted of four mixtures and samples of the single oxides from which these mixtures had been made, all of which had been slowly dried and partially dehydrated, and were in the form of porous granules. In the dis-

[14] Waran, *Phil. Mag.*, [6] 42, 246 (1921).

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[1] (a) Almquist and Bray, THIS JOURNAL, 45, 235 (1923) (on p. 2317, three lines from the bottom of the page, for "Catalyst 2" read "Catalyst 3"). (b) Hoskins and Bray, *ibid.*, 48, 1454 (1926). References to the work of Frazer and his associates, and of other investigators, are given in these papers.

cussion of the "mixture effect" in the catalytic oxidation of carbon monoxide, it was assumed that the two oxides in such mixtures were present as distinct particles in intimate contact with each other. In support of this assumption we are now presenting the results of experiments, completed in 1923, which demonstrate that a mixture prepared by grinding together certain samples of the dry, powdered oxides is much more efficient as a catalyst than either of the constituent oxides.[2]

The catalysts tested were derived from three members of Series 2 of Almquist and Bray: Nos. 1, 6 and 2 which were, respectively, manganese dioxide, $MnO_{1.83}$, copper oxide, and the mixture containing MnO_x and CuO in the proportion of 72 to 28. These were in granular form, and the filter cake from which the granules were made had been dried at 75° for 72 hours. The two single oxides and the mixture are designated Mn°, Cu° and M°.

Mn, Cu and M were powdered samples of these three catalysts. The grinding in an agate mortar was continued for 30 minutes and each powder felt free from gritty material when rubbed between the fingers; 10.5 cc. of M° granules yielded 12.5 cc. of M powder.

Mn′, Cu′ and M′ were powdered samples of the three catalysts which had been heated for 2.5 hours at red heat before being ground to powder.

The four possible mixtures were prepared from the two sets of powdered single oxides by mixing them intimately in the proportion of 72 to 28: MnCu, MnCu′, Mn′Cu and Mn′Cu′.

The method of testing the catalysts was similar to that described by Almquist and Bray,[1a] and the carbon monoxide analyzing device had the modifications recommended by Larson and White.[3] The gas was 0.18 to 0.2% by volume of carbon monoxide in air. The temperature recorded was that of the influent gas, and not that of the catalyst as in the measurements of Almquist and Bray. The difference was found in our first measurements with M° to be 5°, or 6° when 5 cc. of the catalyst was operating at 90% efficiency with 0.2% gas and a space velocity of 5400 (liters per hour per liter of catalyst); which is only 1° greater than the difference reported by Almquist and Bray. This heating effect, of course, would be smaller at lower efficiency or lower space velocity.

In order to make sure that we could obtain reproducible efficiency-temperature curves, several runs were made with 5 cc. of the granular

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[2] Attention must be called to the fact that the mixture effect in this catalysis has been demonstrated only when inactive manganese dioxide has been used in preparing the mixtures, and that Whitesell and Frazer [This Journal, 45, 2841 (1923); see also Ref. 1 b, p. 1471] have prepared very active samples of manganese dioxide. However, it seems important to record the result that a relatively active catalyst can be produced merely by bringing particles of copper oxide and inactive manganese dioxide into intimate contact with each other.

[3] Larson and White, This Journal, 44, 21 (1922).

mixture M°, in a tube of 1 sq. cm. cross section, at a space velocity of 5400. It was found that reproducible results could be obtained rapidly only when the catalyst had been brought into an active condition either by letting it operate at high efficiency or by heating it in a current of dry air, whereby, presumably, a water film was removed from the surface.[4] Accordingly, in the later work, each catalyst was first heated for an hour in a current of dry air. This heat treatment was at 150° when the catalyst operated at 100% efficiency at a lower temperature, and at a higher temperature in other cases. Points on the efficiency-temperature curve were then determined in the order of decreasing temperatures, the temperature being held constant for 30 minutes for a single measurement.

The results with M° at 5400 space velocity were reproducible to 1°. The data given in the first line of Table I were read from a smooth curve. Comparison with the corresponding curve of Almquist and Bray shows that at the same efficiencies our points are 4° or 5° lower (even after allowance is made for the difference in temperature between the gas and the catalyst). The discrepancy is not large, and is probably due to the fact that in this instance the measurements of Almquist and Bray were made in the order of increasing temperatures and were not repeated after the catalyst had operated at 100% efficiency.

TABLE I

CATALYTIC EFFICIENCY OF THE GRANULAR MIXTURE OF TWO-SPACE VELOCITIES. TEMPERATURE AT VARIOUS EFFICIENCIES

Efficiency, %	50	60	70	80	90	100
Space velocity 5400	22°	26°	30°	34°	40°	50°
Space velocity 2700	16°	20°	24°	29°	34°	45°

Two runs with M° were also made at a lower space velocity, 2700, with catalyst volumes of 5 and 10 cc., respectively, in the tube of 1 sq. cm. cross section. The seven points determined in the first case and the three in the second were on the same curve, thus illustrating the well-known fact that the efficiency at a given temperature depends mainly on the space velocity. Some of the experimental points are shown in curve M° in Fig. 1, and the data in the second line of Table I were read from the curve. The results in Table I show that at a given efficiency the temperature of operation is lowered by 5° to 6° when the space velocity is halved.

The powdered catalysts were tested at a space velocity of 2700 in a tube 0.57 sq. cm. in cross section. A 2.5cc. portion of catalyst was used in each run, the powder and glass wool being placed in the tube in alternate layers, each about 1 cm. in depth. The experimental results are plotted in Fig. 1, and summarized in Table II.

The curve for the powdered mixture M coincides with that for the

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[4] See Ref. 1 a, p. 2312 and Ref. 2, Footnote 3.

TABLE II

CATALYTIC EFFICIENCY OF THE CATALYSTS AT 2700 SPACE VELOCITY. TEMPERATURE AT VARIOUS EFFICIENCIES

Efficiency	20%	50%	80%
M°, granular mixture	...	16°	29°
M, powdered mixture	...	16°	29°
M′, powdered after heating M°	111°	165°	230°
[Mn° granular $MnO_{1.83}$ (A. and B. at 5400 s. v.)	118°	138°	156°]
Mn, powdered $MnO_{1.83}$	209°	273°	...
Mn′, powdered after heating Mn°	265°	(330°)	...
[Cu°, granular CuO (A. and B. at 5400 s. v.)	88°	99°	110°]
Cu, powdered CuO	158°	211°	270°
Cu′, powdered after heating Cu°	250°	(310°)	...
MnCu, mixture of Mn and Cu	32°	51°	60°
MnCu′, mixture of Mn and Cu′	(29°)	49°	60°
Mn′Cu, *mixture of Mn′ and Cu*	45°	67°	97°
Mn′Cu′, mixture of Mn′ and Cu′	98°	128°	160°

granular catalyst M°; showing that in this case there was no change in efficiency when the granules were powdered.

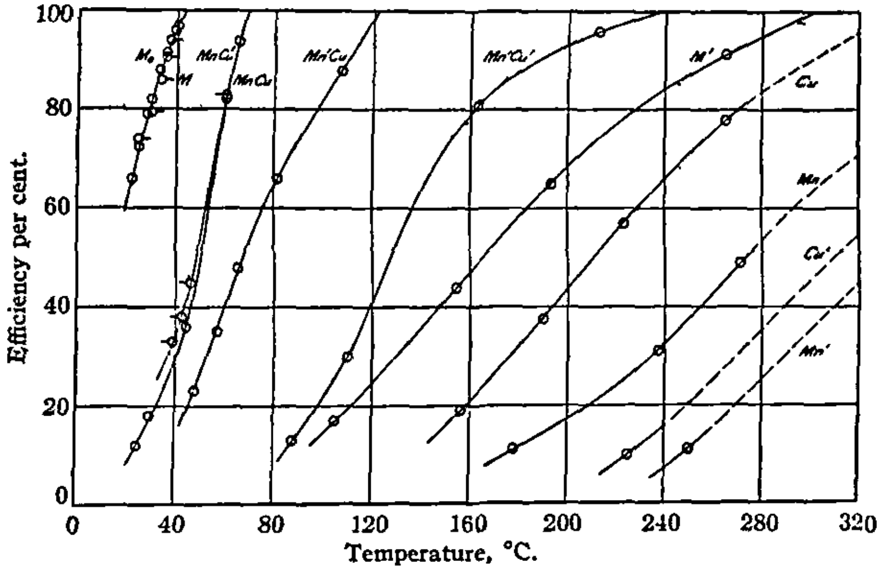

Fig. 1.—Efficiency-temperature curves for powdered catalysts at 2700 space velocity.

This, however, was not true in the case of the single oxides; the powders were found to be much less efficient than the granules. (The latter were not tested at 2700 s. v., but the results of Almquist and Bray at 5400 s. v. are included in Table II.) This marked difference in the effect of powdering the mixtures and the single oxides may be related to the fact that in the latter case the granules are relatively very soft. The grinding may have changed materially the structure of the particles of the single oxides, or the fine, soft powder may have packed in such a way that adequate contact with the gas was not possible.

That the efficiency of these porous, partially hydrated catalysts is greatly lessened by heating has long been known, and is illustrated by our results with powders prepared from strongly heated granules. Thus the temperature at which the catalyst acts at 50% efficiency is increased from 16° to 165° in the case of the mixture (M′), and is over 300° in the case of the single oxides after heating (Mn′ and Cu′). The oxides are dehydrated by the heating, and the structure of the fine particles is altered.

There remains to be considered the behavior of the catalysts prepared by mixing the dry, powdered single oxides. The most striking result is the high efficiency of the two mixtures, MnCu and MnCu′, of which the unheated manganese dioxide powder is the principal constituent. The two curves are nearly coincident, and the temperature at 50% efficiency is 50° ± 1°. Comparison with the curves for the component oxides shows that there is a very great "mixture effect" and, therefore, that this effect depends primarily upon the intimate contact of particles of the two oxides. It is not surprising that the curve for the original mixture, M, is 31° to 34° lower than the curve for these mixtures, since the wet mixing and the drying bring about more intimate contact of the particles.[5]

The third mixture, Mn′Cu, is almost as good a catalyst as either of the preceding mixtures. The fourth, Mn′Cu′, made from the heated oxides, is much less efficient; but it is a somewhat better catalyst than the heated mixture M′. Both show large mixture effects with reference to the constituent oxides.

Summary

Catalysts prepared by grinding together certain samples of the dry powdered oxides, manganese dioxide and copper oxide, have been shown to be much more efficient in the carbon monoxide-oxygen reaction than the constituent oxides.

BERKELEY, CALIFORNIA

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[5] See Ref. 1 a, p. 2321, Footnote 16.

[CONTRIBUTION FROM THE LABORATORY OF FOODS AND SANITATION, UNIVERSITY OF WISCONSIN]

THE VAPOR PRESSURE OF SULFUR MONOCHLORIDE[1]

BY ELLERY H. HARVEY AND H. A. SCHUETTE

RECEIVED APRIL 3, 1926 PUBLISHED AUGUST 5, 1926

Sulfur monochloride seems to have been definitely known since 1803 when Thomson[2] first described it, but in contradiction to this statement is that of Payen[3] who reports that it was first obtained by Hagemann in 1782, although its constitution was not fully ascertained until it was studied by Davy and Bucholz in 1810.

In view of the diversity of directions in which sulfur monochloride finds technical application, it is pertinent to note that a very careful search of the literature failed to disclose any record of vapor-pressure measurements which had been made on highly purified material. It is the purpose of this communication to present such measurements, the heat of vaporization and the molecular elevation which have been calculated from these data.

Experimental Procedure

Materials.—A commercial grade of sulfur monochloride served as the source material from which a highly purified preparation was obtained for use in these measurements. Redistillation is not satisfactory since Thorpe[4] found that under such conditions there is a partial decomposition into the dichloride and sulfur. This observation led Pope[5] to propose a method which yields a pure sulfur monochloride. It is the method of purification used in this investigation.

Sulfur monochloride of "pure" grade was mixed with 1% by weight of highly absorbent charcoal and sulfur. This mixture was distilled under atmospheric pressure in an all-glass apparatus, the fraction distilling above 137° being redistilled in a vacuum after the addition of sulfur and charcoal. Under a pressure of 28 mm., pure sulfur monochloride distilled at 41°. Its golden-yellow color, free from any tinge of red, was indicative of the absence of the higher chlorides of sulfur. It possessed the following physical constants: d_4^{25} 1.67328; surface tension (capillary rise method), 40.78^{22}; relative viscosity, 1.908^{18}.

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[1] Taken from a thesis submitted by E. H. Harvey to the Faculty of the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy, January, 1926.

[2] Thomson, *J. Nat. Philosophy, Chem. Arts* (W. Nicholson), **6**, 92 (1803).

[3] Payen, "Manual of Industrial Chemistry," trans. by Paul, Wiley, 1878, p. 176.

[4] Thorpe, *J. Chem. Soc.*, **37**, 356 (1880).

[5] Pope, *ibid.*, **119**, 634 (1921).

Due precautions were taken to keep the material dry and out of contact with the air.[6]

Apparatus.—Ordinary methods of vapor-pressure measurement cannot be used on sulfur monochloride since it reacts with the mercury of the manometer. Its corrosive nature and susceptibility to decomposition by moisture make imperative the use of an all-glass apparatus. Satisfactory methods for determining the vapor pressures of corrosive liquids have been described within recent years, the method and form of apparatus used by Daniels and Bright[7,8] serving our purposes.

The essential feature of the method consists in the use of a glass diaphragm, sensitive to about 1 mm. pressure, whose movement makes or breaks an electric circuit and permits the balancing of an air pressure against the unknown pressure. The latter is read directly on a mercury manometer.

Experimental Results

Using standard methods of thermostatic control, pressure readings were made at temperatures indicated in Table I. Owing to temperature lag,

TABLE I

VAPOR PRESSURE OF SULFUR MONOCHLORIDE

Temp., °C.	Pressure, mm. of Hg Obs.	Pressure, mm. of Hg Calcd.	$P_{obs.} - P_{calcd.}$
0	3.7	3.7	0.0
10	6.4	6.4	.0
20	10.7	10.8	+ .1
31	18.6	18.6	.0
40	28.0	28.8	+ .8
50	43.0	43.9	+ .9
59	60.0	59.9	− .1
70	93.0	94.1	+1.1
80	135.0	134.6	−0.4
90	186.4	188.7	+2.3
100	257.0	259.8	+2.8
110	351.5	351.8	+0.3
120	469.7	469.0	− .7
130	615.2	615.2	.0
138	760.0	760.0	.0

Mean deviation, ± 0.6 mm.

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[6] A drying agent which offers possibilities here might be found in clean, dry, metallic sodium for it was observed that it does not react with pure, dry sulfur monochloride. We have not verified this observation with experimental proof. Nicolardot [*Compt. rend.*, **147**, 676 (1908)] claims that sulfur monochloride is without action on the alkali metals.

[7] Daniels and Bright, THIS JOURNAL, **42**, 1131 (1920).

[8] Dr. Daniels has improved his original pressure cell in that he has materially simplified the diaphragm without changing the principles involved in its operation. A description of the cell will be published in the near future.

a sufficient interval of time was allowed to elapse after the thermostat had come to the desired point before a reading was made. The latter was then corrected for the "zero" point of the apparatus.

Upon the completion of the first series of measurements, the pressure cell was opened at a point where a constriction had been drawn on the side arm while the latter was covered with rubber tubing to prevent ingress of air. It was then re-evacuated and the vapor pressures were again determined. Criteria for the workability of the method and for complete evacuation of the cell preliminary to making observations of pressures lay in the satisfactory duplication of data. Results are given in Table I.

Col. 3 of the table gives the vapor pressures for the temperatures at which the observations were made, calculated by the equation $\log_{10} P_{(\mathrm{mm})} = 7.4550 - (1880.1/T)$. Thise *mpirical* equation gives the vapor pressure of this compound as a function of the temperature up to 760 mm. Just how far above this pressure the equation is applicable is uncertain in view of the inevitable dissociation of sulfur monochloride into the dichloride and sulfur at sufficiently high temperatures. It is quite probable that this point lies just beyond the temperature at which the monochloride boils. When these data are plotted, a curve is obtained whose regularity is indicative of no dissociation. The measured vapor pressures appear to be normal in every respect. This evidence points to the fact that sulfur monochloride is a well-defined, stable compound up to its boiling point.

The heat of vaporization, calculated with the aid of the Clausius-Clapeyron equation, $L(\mathrm{cal./g.}) = [2.303\ R/M][T_1T_2/(T_2 - T_1)][\log_{10} P_2/P_1]$, is 63.9 calories per gram. In this equation R is the gas constant (1.99), M the molecular weight calculated for the formula S_2Cl_2 and P_2 and P_1 are the vapor pressures corresponding to the absolute temperatures T_2 and T_1, respectively. This calculation may be made most conveniently by multiplying the constant of the equation (1880.1) by the gas constant (1.99) and the conversion factor of logarithms (2.303). Ogier[9] reported a value of 49.4 calories per gram from data determined calorimetrically. It is believed that the results obtained above are more nearly correct for reasons which are emphasized in the calculation of the molecular elevation.

A knowledge of the heat of vaporization makes possible the calculation of another constant. When Orndorff and Terrasse[10] determined the molecular weight of sulfur in sulfur monochloride they had at hand no reliable data for the heat of vaporization of the latter. They calculated its molecular elevation from the boiling point ($138.12°_{760\ \mathrm{mm}}$) as given by Thorpe.[4] They found it to be 52.8, a value which was thought to be very nearly correct, inasmuch as they successfully applied it to the determination of

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[9] Ogier, *Compt. rend*, **92**, 922 (1881).

[10] Orndorff and Terrasse, *Am. Chem. J.*, **18**, 173 (1896).

the molecular weight of triphenylmethane in sulfur monochloride. Application of the formula $K = 0.02\ T^2/L$, in which K is the molecular elevation, T the boiling point on the absolute scale and L the heat of vaporization (63.9) gives the value 52.9 which substantiates that of the above investigators.

Summary

1. The vapor pressure of sulfur monochloride has been determined through the temperature range 0° to its boiling point. The equation for the corresponding curve is $\log P = (7.4550) - (1880.1/T)$.
2. Sulfur monochloride is a stable, well-defined compound at these and intermediate temperatures.
3. The heat of vaporization has been determined and found to be at variance with previously reported values.
4. The molecular elevation agrees with that calculated from boiling-point data by other investigators.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 182]

THE IONIZATION OF WEAK ELECTROLYTES

BY D. A. MACINNES

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Arrhenius' theory that the degree of ionization can be obtained from the conductance ratio, Λ/Λ_0, is now quite generally conceded to be untrue for strong electrolytes, since it involves the assumption that the mobilities of the ions do not change from infinite dilution to the concentration in question. The properties of a large group of strong electrolytes can, in fact, be most readily explained by the theory that they are completely ionized. The decrease in the value of the equivalent conductance with concentration is, almost certainly, due to decrease in the ionic mobilities, caused by an inter-ionic attraction which steadily gains strength as the concentration increases. If, therefore, Arrhenius' method for computing the degree of dissociation is not valid for strong electrolytes, it seems improbable that it can be used without modification for weak electrolytes since, as will be shown below, the ion concentrations can attain values large enough to cause appreciable changes in the mobilities of the ions.

It has appeared to me, however, that a more nearly correct degree of dissociation can be obtained by comparing the measured equivalent conductance with that of an equivalent of the ions *at the same ion concentration*, a quantity which will be represented by Λ_e. Thus the degree of dissociation of acetic acid at 0.01 N may be computed by dividing the Λ value for that concentration by the equivalent conductance of completely dissociated acetic acid at the ion concentration existing in the 0.01 N solution. Now if solutions of hydrogen chloride, sodium chloride and sodium acetate are all completely dissociated, Λ_e for acetic acid can be computed by the simple relation $\Lambda_{e\mathrm{HAc}} = \Lambda_{\mathrm{HCl}} - \Lambda_{\mathrm{NaCl}} + \Lambda_{\mathrm{NaAc}}$, the Λ values all being interpolated for the ion concentration of the solution under consideration. This involves a short series of approximations since the value of Λ_e for the solution must be known before the value of the ion concentration, $C \cdot \Lambda/\Lambda_e$, can be obtained. Plots of Λ as ordinates against $C^{1/2}$ as abscissas were found useful for this interpolation as they give nearly straight lines.

If degrees of dissociation, α, calculated from the relation Λ/Λ_e are substituted in the familiar Ostwald dilution law, $K' = \alpha^2 C/(1-\alpha)$, the values of K' are found to increase with the concentration. This is shown in Col. 5 of Table I, which is based on Kendall's[1] excellent conductance work. However, it must be recalled that although the product $C \cdot \Lambda/\Lambda_e$ gives the correct concentrations of the ions, and $(1-\Lambda/\Lambda_e)C$ that of the undissociated portion, each of these must be multiplied by the appropriate activity coefficient if the law of mass action is to hold. The modified Ostwald dilution law thus becomes,[2] for the acid HA

$$K = \frac{\alpha\gamma_{\mathrm{H}^+} \cdot \alpha\gamma_{\mathrm{A}^-} \cdot C}{(1-\alpha)\ \gamma_{\mathrm{HA}}}.$$

For the undissociated portion the activity coefficient, γ_{HA}, has been assumed to be unity, except as mentioned below, since this portion of the solute carries no charge and is otherwise similar to substances that are nearly perfect solutes in aqueous solution, at least at moderate concentrations. The activity coefficients of the ions γ_{H^+} and γ_{A^-} would be expected to change with ion concentration in very nearly the same manner that the activity coefficients of hydrochloric acid solutions vary with the *total* concentration, since the latter substance is completely dissociated. The mean activity coefficients γ have been computed from the Debye-Hückel limiting equation $-\log \gamma = 0.5\sqrt{C}$ with the exception of values at the higher ion concentrations which were interpolated from the values given by Scatchard.[3] The last column of the table gives values of the expression: $K = \alpha^2\gamma^2 C/(1-\alpha)$. With the possible exception of the figures for acetic acid, the value of K is substantially the same throughout the range of concentrations, being more nearly constant in the more concentrated solutions of the stronger acids where the "ionization constant" computed on the Arrhenius assumptions changes rapidly with the concentration. The agreement of the theory with the computations is the more striking

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[1] Kendall, *J. Chem. Soc.*, **101**, 1275 (1912).

[2] After the computations for this paper were completed I learned that Sherrill and Noyes had independently arrived at this equation, in a paper at that time unpublished

[3] Scatchard, THIS JOURNAL, **47**, 641 (1925).

because in each case an error in any one of four series of conductance measurements will affect the value of the constant. Furthermore the constant K is the only empirical constant obtained from the data. Kendall's[4] computations involve two empirical constants, namely, the value of Λ_0 and the "ionization constant," and even so, the equation based on Arrhenius' assumption fails to fit the data for the stronger acids and the higher concentrations. In my computations the data for the lowest concentrations of

TABLE I

Concn.	Λ	Λ_e	"Ionization constant" $\times 10^4$	K' $\times 10^4$	K $\times 10^4$
ACETIC ACID					
0.07369	6.086	385.7	0.1845	0.1868	*0.1743*
.03685	8.591	386.5	.1851	.1862	*.1755*
.01842	12.09	386.9	.1849	.1857	*.1765*
.009211	16.98	388.1	.1849	.1844	*.1769*
.004606	23.81	388.9	.1851	.1840	*.1775*
.002303	33.22	389.2	.1849	.1838	*.1784*
o-CHLOROBENZOIC ACID					
0.006662	134.6	375.8	12.93	13.31	*12.03*
.003331	174.0	377.5	12.86	13.16	*12.11*
.001666	218.0	378.9	12.84	13.04	*12.23*
.0008327	262.6	380.3	12.84	12.86	*12.22*
.0004163	302.1	381.1	12.79	12.54	*12.16*
3,5-DINITROBENZOIC ACID					
0.003929	175.7	373.2	16.14	16.45	*15.03*
.001860	219.0	374.9	15.99	16.12	*15.08*
.0009822	262.7	376.1	15.94	15.90	*15.04*
.0004922	301.5	377.1	15.99	15.69	*15.05*
CYANO-ACETIC ACID					
0.05946	88.0	372.7	40.0	43.39	*34.9*
.02972	117.0	375.3	39.2	42.64	*34.9*
.01487	152.5	377.9	38.3	40.61	*34.9*
.007435	193.9	380.0	37.8	39.53	*34.9*
.003716	238.7	382.0	37.2	38.68	*35.0*
.001858	282.6	384.0	37.2	38.12	*35.2*
.0009290	320.0	385.4	37.3	37.62	*35.6*
.0004645	347.1	387.0	37.3	36.25	*34.7*
o-NITROBENZOIC ACID					
0.03125	139.7	367.0	67.2	73.11	*59.7*
.01562	179.0	369.8	66.0	70.99	*60.0*
.007812	221.9	372.3	64.5	68.70	*60.0*
.003906	265.0	374.6	63.3	66.81	*59.9*
.001953	303.6	376.2	62.8	65.91	*60.5*
.0009765	333.5	378.7	62.7	63.45	*59.6*

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[4] The values in the columns headed "ionization constant" are from Kendall's paper.

the acids were not used since it would have been necessary to extrapolate the corresponding conductance data for the sodium salts. I have not found other data than those given of sufficient accuracy to test the questions involved in this paper. It seems fitting to express appreciation of the recent, very accurate measurements of the conductance of dilute solutions of hydrochloric acid by Parker,[5] without which these computations would not have been possible.

The only case in which there is a definite trend in the value of the constant K is that of acetic acid in which there is a change of 2.2% from 0.07 to 0.002 N. This is probably due to the fact that the conductance data for the acid and its sodium salt were obtained by different workers.[6] In all the other cases cited Kendall measured both types of data. The trend of the constant for acetic acid is not due to a variation from unity of the activity coefficient γ_{HA}, of the undissociated acid. Using the method and data given by Lewis and Randall[7] for computing this factor from the freezing points of the more concentrated aqueous solutions of the acid it was found that this activity coefficient at 0.07 N is 0.996 and is progressively nearer unity for lower concentrations. This small correction has been applied to values of K in Table I. A similar computation of the values of this coefficient for the other acids should, of course, be made but the freezing-point data are not at present available. In any case it probably differs very slightly from unity. Another factor, called to my attention by Professor George Scatchard, which is sufficient to cause deviations of the magnitude observed, and which must certainly be considered in a complete theory for these solutions, is an effect on the activities of the ions produced by the change of the dielectric constant with the concentration. This change is not known for conducting solutions, but computations based on the Debye-Hückel theory indicate that for substances similar in composition to acetic acid a variation in K of the magnitude and sign of that observed may be expected. Similar effects might be present for the other acids, but the computations given above do not indicate their presence.

Summary

Computations, based mainly on Kendall's measurements, show that the mass law holds for a series of organic acids of various strengths, throughout the complete range of concentrations on which conductance measurements have been made, provided (a) that the degrees of ionization are computed in a manner which allows for inter-ionic attraction, and (b) that the resulting ion concentrations are multiplied by the appropriate activity co-

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[5] Parker, THIS JOURNAL, 45, 2027 (1923).

[6] The published values for the conductance of sodium acetate show a wide divergence. I have used the data of Lorenz and Osswald, *Z. anorg. Chem.*, **114**, 209 (1920).

[7] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., **1923**, pp. 284–290.

efficients. The agreement hitherto found with Ostwald's dilution law, for weak electrolytes and for the lower concentrations of "transition" electrolytes, has been found to be due to a compensation of two effects. Arrhenius' method for computing degrees of dissociation yields too low values, and the activity coefficients have been tacitly assumed to be unity, whereas at all low concentrations such coefficients are less than one.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE LABORATORIES OF GENERAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

PROMOTER ACTION IN HOMOGENEOUS CATALYSIS. III. COBALT SALTS AS PROMOTERS IN THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE BY POTASSIUM DICHROMATE

BY ALFRED C. ROBERTSON[1,2]

RECEIVED APRIL 21, 1926 PUBLISHED AUGUST 5, 1926

In a previous study,[3] wherein hydrogen peroxide was decomposed catalytically by cupric and ferric salts, the cause for the "promotion" effect was demonstrated to be due to the formation of cupric acid by the intermediate compound of this catalysis (ferric acid). The mechanism of promotion was provisionally defined as a change in the path of the catalytic reactions, with a concomitant displacement of the region of the steady state. It was felt that other systems should be studied in order to test this hypothesis more fully. Since no other promoters had been found for the system using ferric salts as a catalyst, a new system was sought. This was found in the catalytic decomposition of hydrogen peroxide by potassium dichromate.

This reaction has been known for some time. As a product of this reaction, there are distinguished two different perchromic acids. The blue perchromic acid has been studied more than the red, probably due to its use in analysis. However, it will not be considered here, since whenever it is formed there is reduction of chromium and the reaction is no longer catalytic.

Schönbein[4] considered the brown color formed when potassium dichromate was added to a hydrogen peroxide solution to be a chromium chromate. Berthelot[5] also held this view, but in addition showed that the reaction is catalytic in character. This was done by means of a calorimetric study, which showed that the heat of the catalytic reaction is 20.8 Calories. The heat of formation of hydrogen peroxide is —21.6 Calories,

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[1] Du Pont Fellow.

[2] Part of a thesis submitted to the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[3] Robertson, THIS JOURNAL, 47, 1300 (1925).

[4] Schönbein, *J. prakt. Chem.*, 80, 257 (1860).

[5] Berthelot, *Compt. rend.*, 108, 24 (1889).

a practically identical value. In addition, Berthelot showed that a given amount of the dichromate decomposed an unlimited amount of the hydrogen peroxide and that there was no reduced chromium present when the concentration of the solution was about 0.0625 *N*. Later, Riesenfeld[6] confirmed the fact that the reaction was catalytic, as did Spitalsky.[7]

This last investigator studied the effect of potassium chromate-dichromate mixtures upon hydrogen peroxide and reported that the chromate was less active than the dichromate and that there was no simple mathematical relation to explain the effect of catalytic mixtures containing these salts. Sometime later, Riesenfeld[8] repeated this work and reported that the effect was the sum of the individual effects.

In preliminary investigations it was found that the reaction was indeed catalytic and gave good unimolecular constants under the conditions which were to be used in the promotion studies. The concentration of hydrogen peroxide was 0.190 *M* and that of the dichromate from 0.25 to 0.75 millimolar. After making the correction for temperature differences, the values obtained checked those of Spitalsky very closely.

The nature of the intermediate is not known definitely, but Schönbeins' chromium chromate seems improbable. Later and more exact work treats almost exclusively of the blue compound formed when acid is present—possibly because of the analytic importance of this substance. However, Riesenfeld's[6] work indicates that there is formed in ammoniacal solution a red salt of the formula $(NH_4)_3CrO_8$, which decomposes in alkaline or neutral solutions giving off oxygen with no reduction of chromium to the tervalent state. For the present, an analogous compound will be assumed to be the intermediate. Nearly all investigators upon the perchromates assume that the chromium in this compound has a valence of seven and not six. In this way it differs from other "per" salts in which the central elements are supposed not to possess a higher valence than the maximum fixed by their position in the periodic classification.[9]

Experimental Methods

The technique of experimentation was practically that followed in the research upon ferric salts, being a gasometric method. Considerably more care was exercised in preparing the reaction flasks, since the solutions were presumably neutral. The flasks were subjected to prolonged steaming in order to remove surface alkali. Another difference

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[6] Riesenfeld, Wohlers and Kutsch, *Ber.*, **38**, 1888 (1905).

[7] Spitalsky, *Z. anorg. Chem.*, **53**, 184 (1907).

[8] Riesenfeld, *ibid.*, **74**, 48 (1912).

[9] This point may be regarded as debatable. It is proposed to determine with Dr. D. M. Yost the valence not only in perchromates but in ferrates, pervanadates and cupric acid, by the method of x-ray absorption used by Lindh [*Compt. rend.*, **172**, 1176 (1921)] and others.

was the concentration of hydrogen peroxide, which was 190 millimolar instead of about 130.

When promoters were used the constants of the reaction were invariably calculated by the graphic method. By using a special plotting board 60 by 75 cm. this was found to be moderately rapid. The use of this method detected anomalies in the system where manganese chloride was used as the promoter, and made it possible to study this system thoroughly. This work will be published later.

The potassium dichromate used as the catalyst was prepared by recrystallizing some of the commercial c. p. product thrice and heating to 150°. A stock solution was prepared, 1 cc. of which was equivalent to 2 millimoles per liter in the reaction flask after dilution in the usual manner; since one-half millimole was the usual concentration, a second stock solution was prepared which gave a concentration of 0.05 millimole per liter. Little trouble was anticipated upon the score of a change in the concentration of the catalyst solutions, a stand that was justified since runs made at the end of the study gave constants which agreed well with those of the first few determinations.

Promotion by Cobalt Chloride

It had been found in preliminary experiments that salts of cobalt, copper, nickel, manganese and cerium, among others, promote the catalytic de-

TABLE I

EFFECT OF COBALT CHLORIDE UPON CATALYSIS OF POTASSIUM DICHROMATE

Concn. of $K_2Cr_2O_7$ Millimole per liter	Concn of $CoCl_2$ Millimoles per liter	K_R	*P. F.*	"*D*"
0.25	0	55	1.00	104 (99)
	1	82	1.49	55 (50)
	5	99	1.80	24 (19)
	10	102	1.85	19 (14)
	20	109	1.98	6 (1)
	40	112	2.04	0 ...
0.50	0	110	1.00	78
	0.1	123	1.12	66
	1	151	1.37	41
	5	184	1.67	11
	10	194	1.76	2
	15	196	1.78	0
0.75	0	154	1.00	84
	0.1	174	1.13	71
	1	203	1.31	53
	5	245	1.59	25
	10	259	1.68	16
	20	284	1.84	0
0.50	10 Ni	134	1.22	
.00	50 Ni	1.8	..	
.00	10 Co	2.5	..	

composition of hydrogen peroxide by potassium dichromate. Cobalt was used for the most extensive work, since its salts do not hydrolyze quite so much as those of copper or manganese. The chloride was chosen because experience has shown that sulfates are very complex both in behavior and constitution.

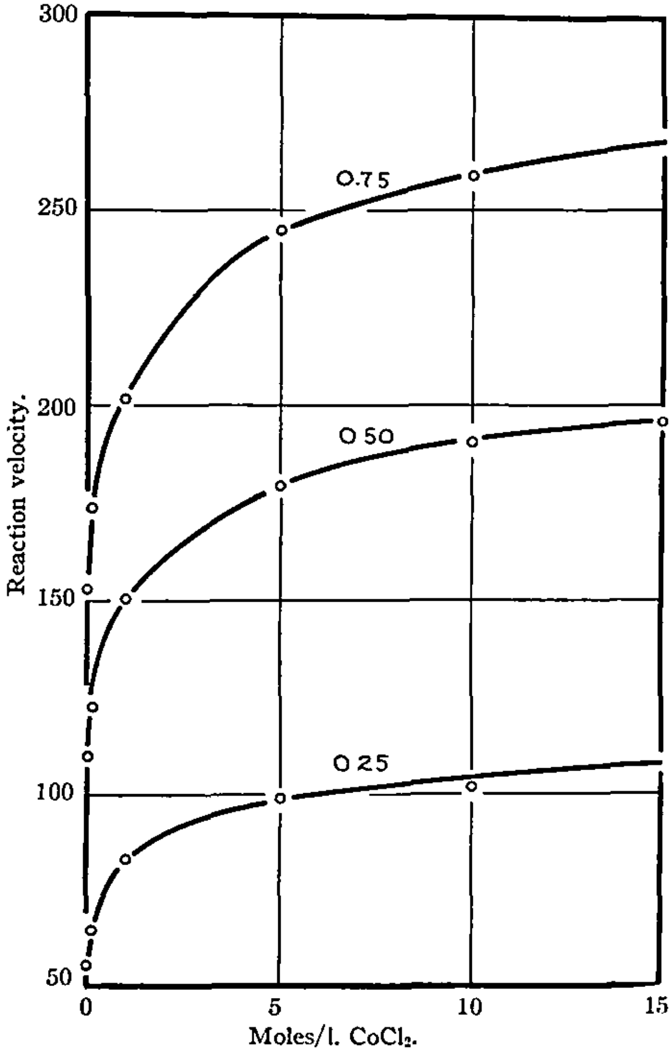


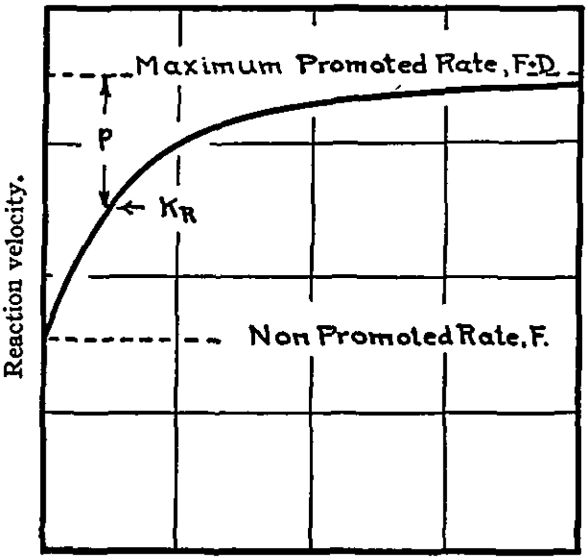
Fig. 1.—Effect of cobalt chloride upon the catalytic decomposition of hydrogen peroxide by potassium dichromate.

A sample of C. P. cobalt chloride was purified by recrystallization from water. The operation was thrice repeated, the last time at a low temperature, since it was found that otherwise some anhydrous blue salt was present. The required amount of the salt was weighed out to give a solution of which 1 cc. represented one millimole per liter. Experiments were run with concentrations of the dichromate of 0.25, 0.50 and 0.75

millimole per liter, without promoter and with various amounts of cobalt chloride. The cobalt chloride was found to be a moderately good promoter, but not so efficacious as the copper as in the case of the ferric salt catalysis. The results of these experiments are shown in Table I and Fig. 1. Several experiments were run with nickel chloride, which is a promoter of the same order as the cobalt, but the work was not investigated further due to the lack of time. A study of this system might be of interest because of the reported isomerism of the higher oxides of nickel.

Discussion of the Promotion Curves

It will be noticed that the curves showing the reaction rate as a function of the amount of added cobalt chloride are smooth with a gradually decreasing slope. They apparently approach a maximum at a decreasing rate and resemble exponential curves where the fractional change is proportional to successive added amounts of promoter. An approximate relationship is obtained when the reaction rate is plotted against the logarithm of the concentration of the promoter. A straight line is obtained which is useful for comparing results and extrapolation. A more exact equation has been developed,[10] but in order to test this relationship it is necessary to know the maximum promoted rate. The log. concn.—reaction rate graph is useful for this purpose.



Concentration of promoter.

Fig. 2.

The explanation of the relationship shown in the equation is very interesting. The conception of activation has been abandoned since experience has shown that it is non-productive and actually misleading. As an analogy to the copper-iron system, the idea presented itself that there probably was the formation of a more highly oxidized compound of cobalt, which is more rapidly auto-reduced by hydrogen peroxide (though less rapidly formed) than the perchromic acid. The application of this idea

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[10] There is another relationship which is felt to be more nearly true but it cannot be easily expressed by a single equation. This relationship will be described in a later paper upon negative catalysis and promoter action with respect to the Steady State.

is best shown by reference to Fig. 2. The rate of the unpromoted reaction is given by F, that of the promoted reaction by F plus D where D is the difference between the rates of reduction of the first and second intermediates as the steady state. For any concentration of the promoter the rate of reaction differs from complete promotion by the amount p. As more promoter is added the amount of p changing is proportional to the amount left unchanged; $—\mathrm{d}p/\mathrm{d}P = k'p$, $—\mathrm{d}p/p = k'\mathrm{d}P$, $—\log p = k'P$; or $p = Ke^{-Pk}$, where in this case D may be set equal to K and the reaction rate expressed in the form, $K_R = F + D - De^{-Pk} = F + D(1 - e^{-Pk})$. F and D may be given in the form of "promotion factors" for convenience in comparing the results of promotion in different systems.

Formation of Cobaltous Acid and the Mechanism of the Reaction

McConnell and Hanes describe the formation of a monohydrated cobalt peroxide, H_2CoO_3, which they call cobaltous acid, by the action of hydrogen peroxide upon cobaltous hydroxide. It is soluble, giving a colorless solution, though solutions of its salts are said to be green. These investigators[11] noted that this substance reacts rapidly with an excess of hydrogen peroxide, though they do not make it clear whether they consider the effect to be purely catalytic, which their equation would indicate, or one of auto-reduction. The latter by analogy with the reactions of copper peroxide seems more logical to the writer.[12]

[11] McConnell and Hanes, *J. Chem. Soc.*, **71**, 584 (1897).

[12] The existence of this compound will be assumed for the purpose of this article, for while the composition of the second intermediate is interesting, it is not vital to the argument. Experiments seeking to prove the composition of this substance have been inconclusive and will be pursued further, together with a study of the chemistry of higher valenced cobalt. This field at present is in a most chaotic condition and the literature is very unreliable. Tervalent cobalt has been found to auto-reduce hydrogen peroxide, but its compounds are nearly impossible to prepare in the pure state, hence its presence has not been determined. A solution of cobaltic sulfate in sulfuric acid is easily prepared and is relatively stable. Its properties were investigated, but the use of this solution in spectrographic studies is rendered questionable, since it seems to the writer that the substance might be a cobaltisulfuric acid analogous to ferrisulfuric acid and have a different absorption of light for that reason. Marshall [*J. Chem. Soc.*, **59**, 760 (1891)] has noted that the alum is far more stable than the cobaltic sulfate alone, and a similar condition may exist here.

However reasonable it is to assume the presence of tervalent cobalt, there is good reason for believing that cobalt with a valence higher than three exists in the reaction mixture. Experiments to be described later show unmistakably that the cobalt produces an acid-forming compound in the promotion reaction. Now, the chemistry of tervalent cobalt is essentially that of a basic element; hence, it is reasonable to assume the presence of some acid-forming higher oxide of cobalt.

Some other higher oxides of cobalt are described in the literature. Since they are insoluble in water and are not formed by hydrogen peroxide, they will not be considered further. A critical review of several papers leads one to think that the product obtained by the action of hypo-iodites and similar reagents upon solutions of cobaltous

The formation of cobaltous acid from the hydroxide probably goes to completion.

$$H_2O_2 + Co(OH)_2 \longrightarrow H_2CoO_3 + H_2O \qquad (1)$$

Where the acid is made from cobalt chloride, the reaction is possibly an equilibrium reaction

$$H_2O_2 + CoCl_2 + H_2O \rightleftharpoons H_2CoO_3 + 2HCl \qquad (2)$$

but both reduction reactions go to completion.

$$H_2CoO_3 + H_2O_2 \longrightarrow Co(OH)_2 + H_2O + O_2 \qquad (3)$$

$$H_2CoO_3 + H_2O_2 + 2HCl \longrightarrow CoCl_2 + 3H_2O + O_2 \qquad (4)$$

Another reaction may accompany the latter

$$H_2CoO_3 + 2HCl \longrightarrow CoCl_2 + 2H_2O + \tfrac{1}{2}O_2 \qquad (5)$$

since the cobaltous acid is unstable in acid solution.

Reactions 2 and 4 together constitute the "catalytic pair" for the decomposition of hydrogen peroxide by cobalt chloride. This is quite a slow reaction, the constant being in the order of 2 for a concentration of 10 millimoles per liter of cobalt chloride.

The reactions for the catalytic decomposition of hydrogen peroxide by the dichromate are written thus:

$$K_2Cr_2O_7 + H_2O_2 \longrightarrow 2KCrO_4 + H_2O \qquad (6)$$

$$2KCrO_4 + H_2O_2 \longrightarrow K_2Cr_2O_7 + H_2O + O_2 \qquad (7)$$

not because the formula $KCrO_4$ represents the composition of the perchromic acid, but because it indicates that the intermediate possesses a higher valence than six.

One would suppose that if a more active oxidizing agent than hydrogen peroxide were used—such as perchromic acid, let us say—the cobalt chloride would be oxidized to cobaltous acid more rapidly than otherwise. The reaction could proceed in the sense of the following reaction,

$$2KCrO_4 + CoCl_2 + 2H_2O \longrightarrow H_2CoO_3 + K_2Cr_2O_7 + 2HCl \qquad (8)$$

with the regeneration of potassium dichromate as one of the reaction products. The cobaltous acid thus produced is rapidly auto-reduced by the hydrogen peroxide, as indicated by Reaction 4, the dichromate forms more intermediate, and so the reactions proceed, the catalytic decomposition as a whole being increased by virtue of this change in path.

The promotion effect may, therefore, be explained as before upon the basis of a change in the path of the reaction. If it is assumed that Reaction 8 is "instantaneous," or a great deal more rapid than Reactions 2, 4, 6 or 7, it is evident that the promoted reaction may be considered as following the path of Reactions 6 and 4 instead of Reactions 6 and 7. Reaction 4 is more rapid than 7 and hence the rate as a whole is increased.

The quantitative consequences of this idea have been developed. The

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salts leads to the formation of insoluble cobaltous cobaltite, which adsorbs the alkali cobaltites and not only removes them largely from solution, but increases the "available oxygen" in the precipitate.

results of the experiments are shown in Table I and Fig. 3. There is a deviation from the straight line which should result, which may be due to the fact that Reaction 8 is so slow that its reaction time is not negligible in comparison with the others.[13] It must be mentioned that in this logarithmic plot the small differences for larger concentrations of promoter are near the limit of experimental error and are greatly exaggerated. For instance, the series for 0.25 millimole of potassium dichromate gives far better results when a maximum promotion factor of 199 is used instead of 204.

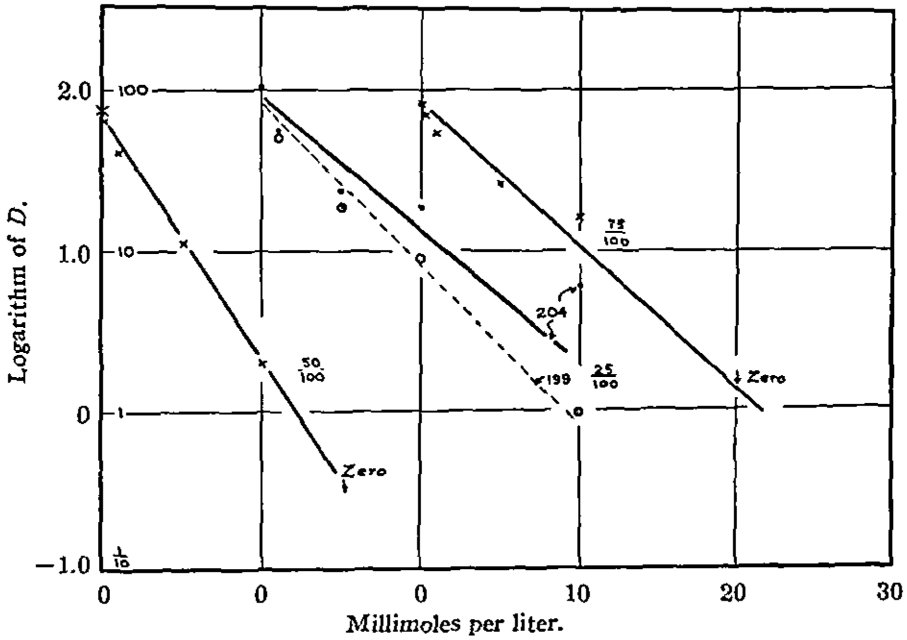

Fig. 3.—Concentration of added $CoCl_2$.

So far the proof follows closely that of a former article[14] and the question of promoter action and the steady state can be considered in an exactly analogous manner which will be apparent by reference to Fig. 5 of that paper.

Effect of Hydrogen Ion Upon the Promotion and the Mechanism of the Promoted Reaction

Due to some peculiarities of this reaction, it was possible to show in another way that the change in the course of the reaction was the cause of the promotion effect. Reaction 4 indicates that acid is necessary during the course of the "reduction" reaction of the catalytic pair for cobalt.

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[13] The results of previous researches upon the promoting effect of copper upon iron salts give good results when thus treated. In that case the reaction analogous to (8) is presumably very fast in comparison with the others.

[14] Ref. 3, pp. 1302, 1309.

This fact suggested that it would be interesting to try the effect of buffer solutions upon the catalytic solutions. The most practical buffer is the sodium acetate-acetic acid mixture. The choice is limited to this because of the range desired and the fact that many other buffer solutions would precipitate the cobalt used as the promoter. Accordingly some non-promoted reactions were carried on in the presence of 100 millimolar sodium acetate and 10 millimolar acetic acid. The reaction velocity was higher than in presumably neutral solutions, being 185 instead of 110. When five millimoles per liter of cobalt was added, the reaction rate was altered very little indeed. A typical log. concn.-time graph is shown in Fig. 4. Instead of being a straight line of about 65% greater slope, that being the promotion factor in the absence of the buffer, it is of the same slope as the non-promoted reaction for the greater part of its course, is nearly coincident and then deviates slightly. This last effect is not easily explained, but probably is due to decomposition of the cobaltous acid with the formation of partially dehydrated cobalt hydroxide or even Co_2O_3, which causes the reaction to be heterogeneous and autocatalytic. When the buffer consists of 100 millimoles sodium acetate and 100 millimoles acetic acid this autocatalytic effect is not apparent, which fact lends support to the idea that the solution is heterogeneous and the solid phase is basic and separates because the solution is not sufficiently acid. In this more acid solution, promotion exhibits itself. However, there is reduction of chromium and it is not practical to study this region further. This autocatalytic effect is most pronounced when sodium acetate is used alone, the solution then being slightly basic. A curve for that condition is also shown in the figure.

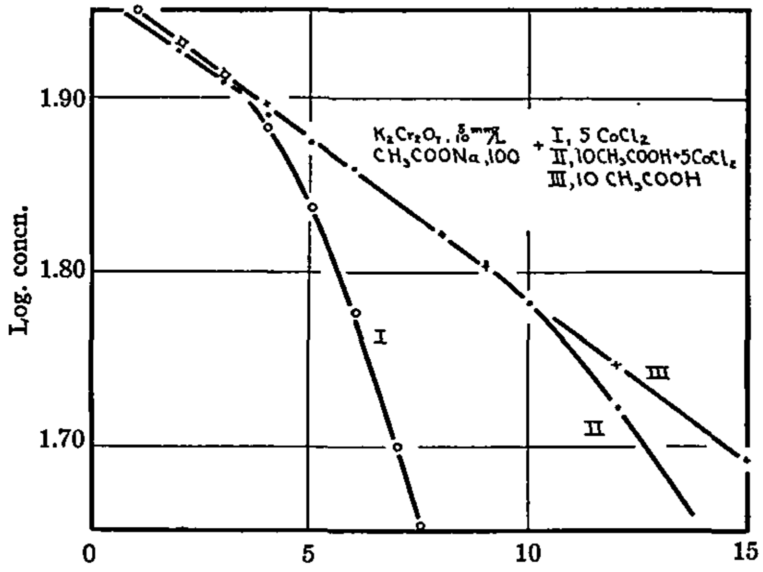

Fig. 4.

From this it may again be concluded that in the promotion here considered, Reaction 4 is the cause of the increase in total reaction rate. A preliminary value of the necessary hydrogen-ion concentration lies between 2.4×10^{-5} and 1.7×10^{-6} equivalent per liter (0.02 and 0.002 millimole per liter), or *P*H 4.6 and *P*H 5.8. It would thus seem that promotion may again be explained upon the basis of a change in the path of reaction. The non-promoted reaction follows the cycle of Reactions 6 and 7, while the promotion effect is due to the cycle through Reactions 6, 8 and 4.

Spectrographic Studies

This hypothesis concerning the change in path is supported by studies of absorption spectra of promoted and non-promoted reactions. The determinations were made with a Gaertner spectrometer equipped with a dense prism and calibrated by the flame spectra of compounds having suitable wave lengths. A Tungsarc lamp was used as a source of light for a Nutting photometer made by Hilger. The results are plotted with Bunsen's extinction coefficients as ordinates against the wave length in Ångström units as abscissas.

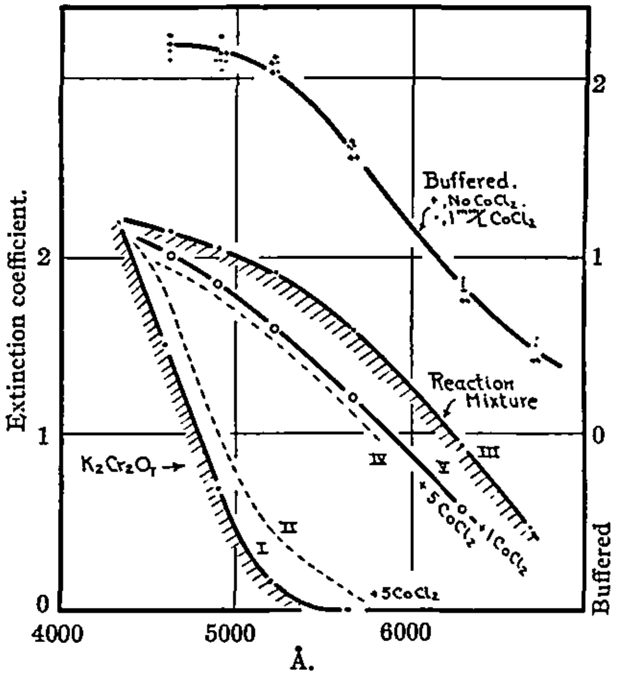

Fig. 5.

Curve I in Fig. 5 shows the absorption due to solutions of potassium dichromate. This is identical with the same solution containing buffer mixtures of one millimole per liter of cobalt chloride. The presence of more cobalt is apparent, as in Curve II, which represents a solution containing 5 millimoles per liter. Upon the addition of hydrogen peroxide to the dichromate solutions the absorption increases as shown in Curve III. However, if cobalt is present Curves IV and V illustrate the results. It is apparent that less of the "first intermediate" is present in the promoted reactions. Indeed, measurements indicate that for one millimole per liter of added cobalt about 30% is removed, the extinction coefficient being roughly proportional to the concentration of the intermediate as shown by separate experiments not recorded here.

In a buffered solution containing 100 millimoles of sodium acetate and 10 millimoles of acetic acid per liter, which shows no promotion in kinetic experiments, there was no change in the concentration of the first intermediate as indicated by the absorption spectrum measurements. This fact confirms the view that Reaction 4 is the basis of the promotion effect. Studies made upon the cobalt-rich portion of the system are so far inconclusive in identifying the second intermediate for reasons noted before, but are being continued in hope of success. By an extension of this method, absolute values may yet be obtained for the amount of hydrogen peroxide going through the more rapid reactions.

The major portion of this work was done at the University of Wisconsin with Professor J. H. Walton, whom the writer wishes to thank for his kindly help and interest in the problem. The material was arranged for publication and the spectrographic studies were made while the author was at the California Institute of Technology as a National Research Fellow.

Summary

1. Promotion has been studied in the catalytic decomposition of hydrogen peroxide by potassium dichromate. Cobalt chloride was used in this study, though salts of copper, nickel, manganese and cerium among others will show this effect.

2. The promotion is an exponential function of the amount of cobalt chloride added.

3. This fact has been explained upon the basis of a change in the path of the catalytic reaction. Oxidation of the cobalt is indicated by a decrease in the concentration of perchromic acid in the promoted reactions. It is not yet possible to say whether the cobalt is in the ter- or quadrivalent form during the promotion.

4. A definite hydrogen-ion concentration is necessary for promotion in this system, as is shown by studies of absorption spectra and by kinetic measurements. This fact is in agreement with the mechanism adopted to explain the promotion.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE LABORATORY OF GENERAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE CATALYTIC INFLUENCE OF FERRIC IONS ON THE OXIDATION OF ETHANOL BY HYDROGEN PEROXIDE

BY JAMES H. WALTON AND CARL J. CHRISTENSEN

RECEIVED MAY 10, 1926 PUBLISHED AUGUST 5, 1926

Although solutions of hydrogen peroxide containing ferrous salts (Fenton's reagent) have long been used for oxidizing sugars, alcohols and other organic compounds,[1] there is comparatively little information on the conditions influencing such oxidations. Much confusion exists concerning the applicability of ferric salts and, further, little attention has been paid to the control of the acidity of the solution, a factor that recent investigation has shown to be of utmost importance.[2]

The object of this investigation was to study the conditions under which Fenton's reagent may best be used and at the same time to throw some light upon the mechanism of the reaction.

Experimental Part

The Reaction.—It was shown by Bohnson[3] that hydrogen peroxide oxidizes ethanol in the presence of ferric salts. Preliminary experiments showed that while hydrogen peroxide and ethanol undergo no appreciable reaction without a catalyst, in the presence of ferric salts the ethanol is completely oxidized to acetic acid without perceptible formation of aldehyde.

Materials.—The ethanol was dehydrated by the usual methods. A specific-gravity test showed it to be practically absolute. All salts were recrystallized at least once. "Perhydrol" (30% by volume hydrogen peroxide) was used as the source of hydrogen peroxide.

Method.—The reaction was followed by titrating the acetic acid formed during various time intervals using phenolphthalein as the indicator, with standard alkali solution. Since hydrogen peroxide is catalytically decomposed by iron salts[3] the active mass present at any given time could not be calculated from this titration; consequently, it was necessary to parallel the acetic acid titrations with permanganate titrations for the peroxide.

In all of the following experiments the volume of the solution was 172 cc. This contained 2 cc. of pure ethanol (0.2 millimole per cc.) and concentrations of hydrogen peroxide, catalyst and acid recorded in the tables. The temperature of all experiments was 35°.

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[1] Fenton, *Chem. News*, **33**, 190 (1876); **43**, 110 (1881); *J. Chem. Soc.*, **65**, 899 (1894); **75**, 1 (1899); **77**, 69 (1900); *Proc. Chem. Soc.*, **15**, 224 (1899).

[2] Hatcher, *Trans. Royal Soc. Canada*, **47**, 119 (1923). Hatcher and Holden, *ibid.*, **48**, 231 (1924).

[3] Bohnson, *J. Phys. Chem.*, **25**, 19 (1921).

Before the reaction started, all of the solutions used contained an original concentration of acid, this being furnished in part by the hydrolysis of the catalyst and in part by acid added to the solution. As a consequence it was necessary to correct the acid titration's values for the concentration of acid present before the oxidation of ethanol began. A correction was also made for the alkali used to precipitate the catalyst as ferric hydroxide.

A sharp end-point was obtained in the acid titration at the beginning of the reaction, but near the end, when practically all the alcohol had been oxidized, the end-point was indistinct and the acid value less than it should be. This was shown to be due to the oxidation of acetic acid to carbon dioxide, a reaction that does not take place, however, until the ethanol is almost completely oxidized, as will be shown later. As a consequence of this reaction, the titrations made near the end of the reaction are untrustworthy.

From the titration values it was possible to calculate at any given time (1) the total number of millimoles of active oxygen given up by the peroxide and (2) the millimoles of ethanol oxidized to acetic acid. If all of the oxygen thus liberated were used to oxidize the ethanol, the number of millimoles of ethanol oxidized in a given period would equal the number of millimoles of oxygen liberated. Since some of the peroxide is decomposed catalytically by the iron salts, the above-mentioned conditions are never realized. The ratio of ethanol oxidized to the decrease in the hydrogen peroxide concentration will be called the "efficiency" of the reaction, or Efficiency = (millimoles of ethanol oxidized)/(millimoles of oxygen evolved).

Reaction Velocities.—According to evidence to be given later, the two reactions, decomposition of the peroxide and oxidation of ethanol, tend to be unimolecular. This is not strictly true under all conditions, however; hence for purposes of comparison first order constants are calculated for the second 25% of the oxidation of the ethanol, during which period the reactions were most free from disturbing factors. The time for the second 25% of the two reactions was determined by plotting the curve for the reaction and interpolating for the time (t) over the region specified. A simple calculation shows that the first-order velocity constant can be obtained by dividing 0.406 by this time for the second 25% of the reaction. Mention has been made of the fact that the reactions measured are not strictly first order. This was made very apparent by plotting the logarithm of the concentration of ethanol against the time. In unimolecular reactions the resulting curve should be a straight line. In those solutions in which the acid added was present in rather high concentration (0.324) this was found to be true. The divergence from unimolecularity probably bears some relation to the increase in acid concentration resulting from the oxidation of ethanol. In those solutions that were strongly acid at the beginning of the experiment, the change in acidity would be relatively less than in the weakly acid solutions.

Effect of Acids on the Reaction.—The speed of oxidation of ethanol and the catalytic decomposition of the hydrogen peroxide in the presence of fixed concentrations of iron salts was measured in solutions containing various amounts of the hydrochloric, nitric, sulfuric and acetic acids. The data for the oxidation of ethanol in the presence of several iron salts are given in Table I and shown graphically in Fig. 1. In all tables the velocity constant K is 1000 times the value calculated. In those solutions to which no acid was added a small amount of basic salt always separated. This precipitate does not catalyze the reaction and its formation decreases the concentration of the ferric ions; consequently, these experiments are slower than the others. In all cases increase in acid concentration decreases the speed of the oxidation of ethanol to acetic acid. In solutions of the same normality, sulfuric acid shows the greatest retarding effect, followed by hydrochloric, nitric and acetic in the order given. From these data the most favorable condition for the rapid oxidation of the ethanol is to have just enough acid in the solution to keep the iron salt from precipitating as a result of hydrolysis.

TABLE I

EFFECT OF ACIDS ON THE REACTION

Concn. of catalyst in each case, 0.005 mole of iron per liter; that of ethanol, 0.2 N. The concentrations of the acids are expressed as normality.

1. $FeCl_3$ and HCl. Initial concn. of H_2O_2 = 0.61 mole per liter.

Concn. acid	0	0.0054	0.016	0.027	0.054	0.081	0.162	0.324
K (C_2H_5OH)	47.7	72.5	48.4	33.3	15.5	9.7	4.5	1.0
K (H_2O_2)	34.6	60.5	41.8	25.6	12.9	8.1	5.1	4.1

2. Fe $(NO_3)_3$ and HNO_3. Initial concn. of H_2O_2 = 0.67 mole per liter.

Concn. acid	0.021	0.042	0.063	0.084	0.104	0.167
K (C_2H_5OH)	50.7	27.0	18.5	13.1	11.7	6.4
K (H_2O_2)	38.0	21.4	13.7	9.2	8.1	5.4

3. $FeSO_4$ and H_2SO_4. Initial concn. of H_2O_2 = 0.55 mole per liter.

Concn. acid	0	0.005	0.0059	0.0273	0.0496	0.104
K (C_2H_5OH)	12.2	24.4	20.1	9.5	5.0	2.5
K (H_2O_2)	10.4	22.0	18.3	7.8	4.5	2.2

4. $FeCl_3$ and CH_3COOH. Initial concn. of H_2O_2 = 0.67 mole per liter.

Concn. acid	0.029	0.074	0.118	0.191
K (C_2H_5OH)	67.8	50.2	38.7	26.2
K (H_2O_2)	50.8	36.0	28.4	22.0

5. $Fe_2(SO_4)_3$ and H_2SO_4. Initial concn. of H_2O_2 = 0.63 mole per liter.
For 0.0164 N acid: K (C_2H_5OH) = 11.8; K (H_2O_2) = 9.4.

6. $FeSO_4.(NH_4)_2SO_4$ and H_2SO_4. Initial concn. of H_2O_2 = 0.61 mole per liter.
For 0.0114 acid: K (C_2H_5OH) = 16.5; K (H_2O_2) = 12.6.

Efficiency of the Reaction.—Table II gives the efficiency of the oxidation of ethanol using different catalysts in equivalent concentrations and different concentrations of acid. The results are expressed as "per cent. efficiency" which is the ethanol actually oxidized compared with the ethanol that would have been oxidized if there had been no catalytic decomposition of hydrogen peroxide.

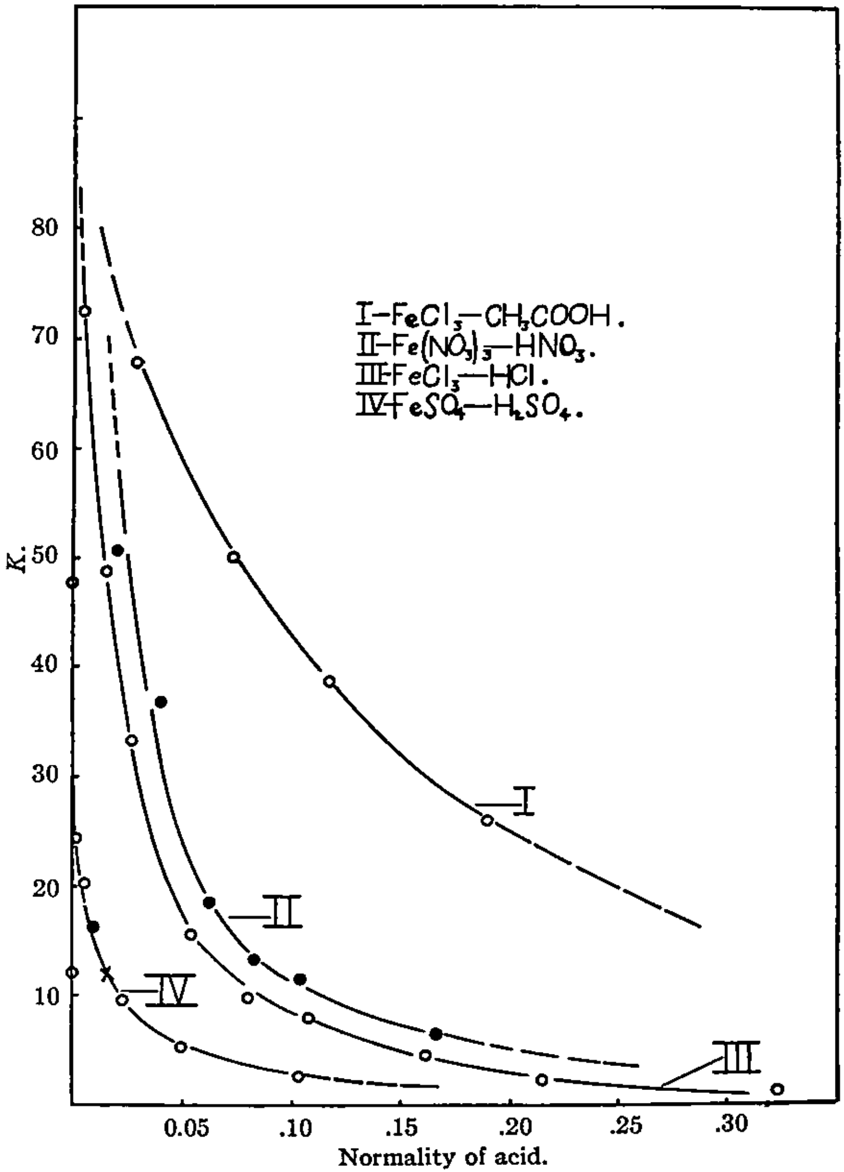

Fig. 1.—Effect of acids on velocity of oxidation of ethanol.

Hydrochloric Acid with Ferric Chloride.—The efficiency drops off when the concentration of the acid is greater than 0.027 *N*. This is undoubtedly due to the fact that hydrochloric acid is a catalyst for hydrogen

TABLE II

EFFICIENCY OF THE REACTION

				Per cent. efficiency for		
Catalyst[a]	Acid	Acid, *N*	Moles of H_2O_2 per liter	First 10 millimoles of oxygen evolved	First 20 millimoles of oxygen evolved	First 35 millimoles of oxygen evolved
$FeCl_3$	HCl	0 to 0.027	0.61	58	64	71
		0.054	.61	49	57	66
		.081	.61	40	47.5	56
		.108	.61	33	40	44
		.162	.61	25	30	41
		.324	.61	20	25	30
$Fe(NO_3)_3$	HNO_3	0 to 0.167	.67	47.5	58.8	71
$FeSO_4$	H_2SO_4	0 to 0.109	.55	60.0	71.0	79
$FeCl_3$	$HC_2H_3O_2$	0 to 0.191	.67	50.0	61.0	70
$Fe(NO_3)_3$	HNO_3	0.024	1.79	60.0	59.0	60.7

[a] Concentration of catalyst in each case 0.005 mole of iron per liter.

peroxide[4] and this substance is being decomposed by both the ferric chloride and the hydrochloric acid. The ferric salt, however, is the only catalyst for the oxidation of the ethanol. The catalytic influence of hydrochloric acid is further evident in Fig. 2, where the catalytic decomposition of hydrogen peroxide is slightly more rapid in the nitric acid than the hydrochloric acid solutions of low acid concentration. As the concentrations of the acids increase, however, the speeds of the reactions in the two solutions approach each other and there is little doubt that at higher concentrations the speed in the hydrochloric acid would exceed that in the nitric acid solution. No such relationship is seen in the oxidation of ethanol, Fig. 1; the curves parallel each other over the entire range.

Nitric Acid with Ferric Nitrate.—While an increase in the concentration of this acid cuts down the rate of the two reactions, the efficiency is constant throughout the range of concentrations, and approximates the efficiency of hydrochloric acid systems of 0.027 *N*.

Sulfuric Acid with Ferric and Ferrous Salts.—The salts used were ferrous sulfate, ferric sulfate and ferrous ammonium sulfate. The two types of salts were used because of the statement that the ferrous salts only are effective in Fenton's reagent. If the assumption is made that the ferrous salt is at once oxidized by the hydrogen peroxide according to the equation $2FeSO_4 + H_2O_2 + H_2SO_4 = Fe_2(SO_4)_3 + 2H_2O$, it is evident that in comparing the effect of acid in the presence of the two salts a correction must be made for the acid used up in the oxidation of the ferrous salt. The data given have been corrected accordingly. The lower curves of Figs. 1 and 2 show that the velocity constants for these three salts are in agreement, for they all fall on the same general curve; in other words, in

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[4] Maass and Hiebert, THIS JOURNAL, **46**, 290 (1924). Livingston and Bray, *ibid.*, **47**, 2069 (1925).

this reaction the state of oxidation of the iron in Fenton's reagent is immaterial. The efficiency of the system is independent of the concentration of the sulfuric acid and is of the same order as the nitric acid though the table shows a slightly higher value. This is undoubtedly due to the fact that the initial concentration of hydrogen peroxide is lower than that in the nitric acid solutions. This effect will be considered later.

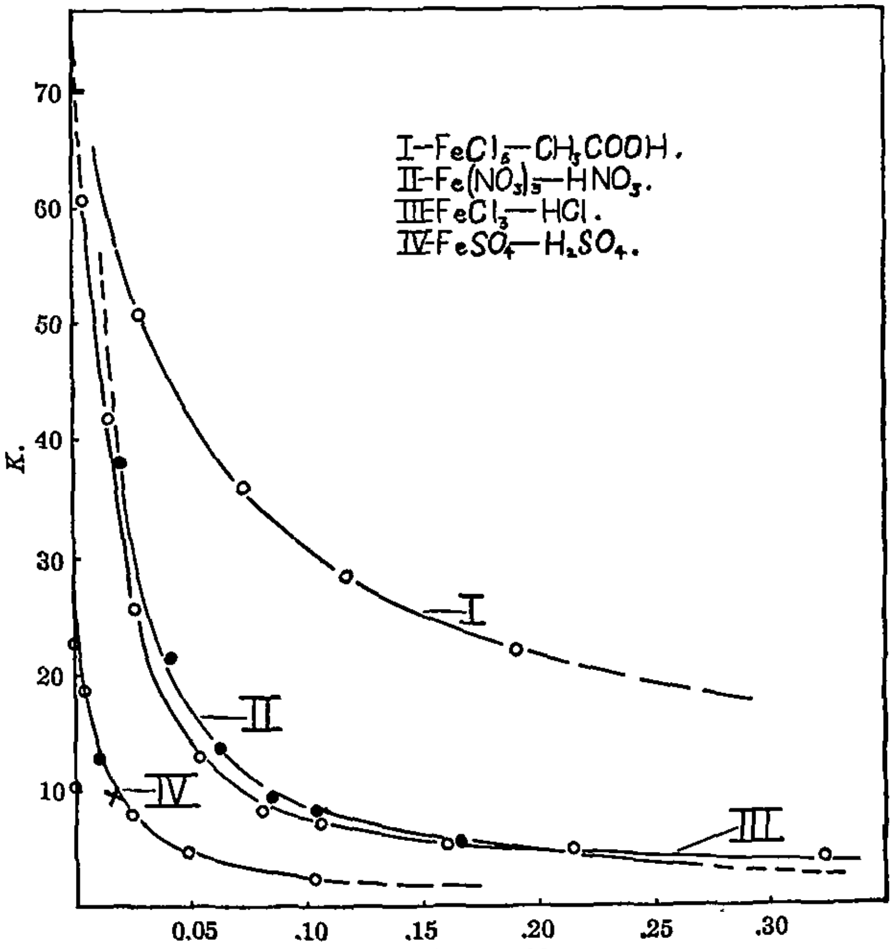

Fig. 2.—Effect of acids on velocity of decomposition of hydrogen peroxide.

Acetic Acid and Ferric Chloride.—Acetic acid does not retard the two reactions as much as the other acids, but the efficiency is about the same as that of the sulfuric and nitric acid solutions.

Comparison of the Different Acids.—The data in Table II show that the efficiency of this reaction increases as the concentration of the hydrogen peroxide decreases. Further, the efficiency, except in the case of the solutions of hydrochloric acid above 0.027 *N*, is independent of the acid, the acid concentration and the iron salt used as a catalyst.

In a study of the catalytic decomposition of hydrogen peroxide by ferric salts Bohnson found that increasing the acidity of the solution decreased the activity of the iron salts. This has been explained as follows. The hydrogen peroxide oxidizes the ferric salt to ferric acid, which is then reduced to ferric iron by the excess of hydrogen peroxide as follows.

$$2FeR_3 + 3H_2O_2 + 2H_2 \rightleftharpoons H_2FeO_4 + 6HR \quad (1)$$

$$2H_2FeO_4 + 3H_2O_2 \longrightarrow 2Fe(OH)_3 + 2H_2O + 3O_2 \quad (2)$$

$$2Fe\ (OH)_3 + 6HR \rightleftharpoons 2FeR_3 + 6H_2O \quad (3)$$

The existence of the ferric acid has been conclusively demonstrated by Bohnson and Robertson[5] by means of spectrographic studies. From Equation 1, it is evident that an increase in the concentration of the acid would decrease the concentration of ferric acid, thus explaining the retarding effect of acids.

The fact that both oxidation of ethanol and decomposition of peroxide are retarded by acids suggests ferric acid as the same intermediate in both cases. In this case one would expect that change in the concentration of the intermediate would affect the two reactions in a similar manner. That this is the case will be seen by comparing the curves in Fig. 1 with those in Fig. 2. With the exception of the $FeCl_3$-HCl solutions, whose discrepancy has been explained, these curves parallel each other throughout. It is therefore concluded that the ferric acid is the intermediate in the oxidation of ethanol by Fenton's reagent. Whether or not this holds in other oxidations by Fenton's reagent will be the subject of further investigation.

Effect of Concentration of Catalyst.—Using ferric nitrate in nitric acid as a catalyst, the data given in Table III were obtained. The constancy of the values in the last two columns shows that the speed of the two reactions is directly proportional to the concentration of the catalyst used.

TABLE III

RELATION BETWEEN THE CONCENTRATION OF CATALYST ($Fe(NO_3)_3$) AND SPEED OF THE REACTION

Acid concentration: 0.0417 *N* HNO_3. H_2O_2 concentration: 0.60 mole per liter

Concn. of $Fe(NO_3)_3$, moles per liter	$K(C_2H_5OH)$	$K(H_2O_2)$	$\frac{K(C_2H_5OH)}{\text{Concn. } Fe(NO_3)_3}$	$\frac{K(H_2O_2)}{\text{Concn. } Fe(NO_3)_3}$
0.001	5.7	4.2	0 0057	0.0042
.005	36.9	25.4	.0074	.0051
.010	72.5	58 0	.0073	.0058
.015	109.8	88.4	.0073	.0059
.020	156.1	119.5	.0073	.0060

Effect of Increasing the Concentration of Hydrogen Peroxide.—The concentration of the peroxide was almost thrice that used in the

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[5] Bohnson and Robertson, THIS JOURNAL, 45, 2493 (1923).

previous experiments. Ferric nitrate was used as a catalyst. The value of K for oxidation of ethanol was 162 compared with 50.7 in the dilute solutions of the peroxide. After the ethanol was completely oxidized to acetic acid a large excess of peroxide still being present, the acidity of the solution began to decrease due to oxidation of acetic acid to carbon dioxide and water. The carbon dioxide was swept out of the solution by the oxygen that was continuously evolved, so that the end-point obtained while following the reaction by titration with alkali was sharp at all times. Plotting the logarithm of the concentration of the acid against the time gave a curve with a very sharp break, which showed that the oxidation of the acetic acid follows the oxidation of the ethanol. This break is indicated in the following data obtained from duplicate experiments in which the oxidation of the ethanol and subsequent oxidation of acetic acid were followed by titrating samples of the solution with approximately 0.1 N potassium hydroxide solution.

t, min	29	62	97	132	167	198	230	328	443	879
KOH, cc	3.0	6.5	9.9	10.1	9.1	8.4	8	7	6.5	5.5

The efficiency of this experiment is constant (Table II). The data in Table II show that in experiments with very dilute solutions of hydrogen peroxide the efficiency approaches 100%, but at higher concentrations of peroxide it remains constant at about 60%.

Effect of Copper as a Promoter.—Bohnson and Robertson[5] have shown that copper ions promote the decomposition of hydrogen peroxide by ferric ions. Robertson[6] has shown that the copper ions function as follows. Ferric acid is formed which reacts with the copper thus: $3CuO + 2FeO_3 = 3CuO_2 + Fe_2O_3$. The CuO_2 (cupric acid), a new intermediate formed only in the presence of ferric acid, reacts very much more energetically in a mutual reduction with hydrogen peroxide, than the ferric acid. In view of these facts it was of interest to investigate the effect of copper salts on the oxidation of ethanol by Fenton's reagent. In no case was promoter action observed in the oxidation of ethanol but the decomposition of hydrogen peroxide was greatly accelerated.

Other Salts as Catalysts.—A number of other salt catalysts were used in place of the iron salt in the application of hydrogen peroxide in oxidizing ethanol but no one of them approached the iron as a catalyst. Of those tried, sodium vanadate was the best, with potassium chloroplatinate a close second. The other substances used were cobalt chloride, nickel chloride, sodium molybdate, uranium nitrate, manganese chloride, manganese acetate, chloroplatinic acid, sodium tungstate, cerium chloride, potassium dichromate and sodium borate. Certain experimenters have stated that manganese salts are good catalysts in oxidations with atmos-

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[6] Robertson, This Journal, 47, 1299 (1925).

pheric oxygen. With the hydrogen peroxide, however, they are comparatively ineffective.

Summary

1. Hydrogen peroxide in the presence of ferric salts (Fenton's reagent) oxidizes ethanol to acetic acid. The reaction is quantitative. This reaction is paralleled by the catalytic decomposition of the hydrogen peroxide by the ferric ions. The two reactions are approximately unimolecular.

2. Acids retard the speed of these reactions. In solutions of equivalent concentrations the order of increasing effectiveness is acetic, nitric, hydrochloric, sulfuric.

3. The speed of the two reactions is directly proportional to the concentration of the catalyst.

4. The reaction velocity increases with the concentration of the hydrogen peroxide.

5. Ferrous salts have been shown to be just as effective as ferric salts, inasmuch as they are immediately oxidized to the trivalent condition.

6. Evidence has been obtained that the ethanol is oxidized through the formation of ferric acid as an intermediate.

7. The oxidation of the ethanol to acetic acid is followed by the oxidation of the acetic acid to carbon dioxide and water.

8. Other salts substituted for the ferric compounds in Fenton's reagent have been found to be unsatisfactory.

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[Contribution from the Chemical Laboratory of the Johns Hopkins University]

CATALYSIS IN BUFFER SOLUTIONS. I

By Martin Kilpatrick, Jr.[1]

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The general purpose of this work was to study the velocity of various reactions in small concentrations of hydrogen and hydroxyl ions. The study necessitated the use of buffer solutions and a consideration of the effect of neutral salts. A preliminary study indicated that with certain limitations several reactions are suitable for the purpose: (1) the decomposition of nitrosotriacetoneamine; (2) the decomposition of diazoacetic ester; (3) the reaction between acetone and iodine as catalyzed by hydrogen ion; (4) the mutarotation of sugars; (5) the hydrolysis of the esters. The last two reactions are catalyzed by both hydrogen and hydroxyl ions and permit a study of the catalytic minimum point.

The present paper deals with the decomposition of nitrosotriacetoneamine, catalyzed by hydroxyl ions. The reaction has been studied by

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[1] National Research Fellow.

Francis[2] and his students, and more recently by Brönsted[3] and King. Francis found the reaction to be complicated at concentrations of hydroxyl ion above 0.05 *N*. With small concentrations of hydroxyl ion the reaction appears to be a simple decomposition catalyzed by hydroxyl ion. Francis' results indicated that below 0.2 *N* total equivalent salt concentration the salt effect would be negligible for the work contemplated. The recent results of Brönsted and King show a salt effect for 0.01 *N* sodium hydroxide solution at 15° amounting to 7% in 0.1 *N* salt solution. The suggestion was made that this higher salt effect might be due to the lower concentrations and temperature. In order to clear up these apparent discrepancies, and to determine the temperature coefficient more accurately, the study of the reaction velocity in dilute solutions of sodium hydroxide was continued before the study in buffer solutions was undertaken.

The rate of reaction can be followed conveniently by measuring the volume or the pressure of the gas evolved. The pressure method is not readily applicable to high temperatures and consequently the volume method was adopted. In either case the most important point is "to agitate the solution to such an extent that the gas is registered on the volume- (or pressure-) measuring apparatus as soon as it is formed in the solution."[4] The importance of this factor has been emphasized by recent work on supersaturation.[5]

Experimental Method

Florence flasks were fitted with rubber stoppers through which passed mercury-sealed stirrers with outlets attached; the stirrers were a modified form of that described by Reid.[6] The shaft was fitted with a detachable glass stirrer of the Witt type with two extra prongs to break the surface of the liquid. For work up to 40° the temperature was controlled within 0.01° by two electrically regulated thermostats. The differences in temperature between the reacting solutions and the baths, due to stirring, were avoided in the long-time experiments by shutting off the stirrers between readings. For the work at 60° and at 80° double-walled vapor-baths of chloroform and of benzene were used as thermostats.

To carry out an experiment, the solution of the buffer mixture or base was siphoned into the reaction vessel which was stoppered and placed in the thermostat. When the solution had come to temperature a weighed amount of the nitrosotriacetoneamine was added, the stirrer inserted, and

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[2] Francis and Clibbens, *J. Chem. Soc.*, **101**, 2358 (1912). Francis and Geake, *ibid.*, **103**, 1722 (1913). Francis, Geake and Roche, *ibid.*, **107**, 1651 (1915).

[3] Brönsted and King, THIS JOURNAL, **47**, 2523 (1925).

[4] Harned, *ibid.*, **40**, 1464 (1918).

[5] Findlay and students, *J. Chem. Soc.*, **103**, 1170 (1913); **105**, 1297 (1914); **121**, 1046 (1922). Metschl, *J. Phys. Chem.*, **28**, 417 (1924).

[6] Reid, THIS JOURNAL, **37**, 2112 (1915).

the outlet connected to the gas buret. After the stirrer had thoroughly mixed the solution, and 1 or 2 cc. of gas had been given off, the buret reading and the time were taken. Readings were taken at suitable intervals and the reaction was allowed to run to completion when the final reading was made. In the preliminary experiments it was found necessary to exclude oxygen as well as carbon dioxide, so all experiments were run in an atmosphere of nitrogen.

The velocity constants were calculated by the equation $k = (2.30/t)(\log v_\infty - v_0/v_\infty - v_t)$, where v_∞ is the final reading, v_0 the initial and v_t the reading at time t.

Preliminary experiments showed that stirring above 1500 r.p.m. gave reproducible results which were unaltered at speeds as high as 4000 r.p.m.

Table I gives the results of a series of experiments at 30° for various concentrations of reactants. The last column is included for the sake of comparison with the data of Francis. His $k/[\mathrm{OH}^-]$ value, calculated in the same way, was 1.92.

Table I

Decomposition of Nitrosotriacetoneamine in NaOH Solutions

R.p.m.	Approx. molarity nitroso-amine	Normality NaOH	k	$k/[\mathrm{NaOH}]$	$k/[\mathrm{OH}^-]$
1500	0.006	0.006190	0.0115	1.86	1.91
2000	.017	.006190	.0116	1.87	1.92
3000	.006	.005420	.01005	1.85	1.90
1500	.006	.005420	.00957	1.77	1.81
4000	.022	.01542	.0274	1.78	1.85
1500	.022	.01542	.0273	1.77	1.84
4000	.015	.01000	.0182	1.82	1.89
2000	.015	.02250	.0397	1.77	1.86
4000	.015	.02250	.0414	1.84	1.94
2000	.015	.01110	.0202	1.82	1.89
1500	.015	.002585	.00493	1.91	1.95
3000	.015	.002585	.00500	1.93	1.97
3000	.015	.01760	.0313	1.78	1.87
					Av. 1.89
					a. d., 2%

To check the work of Brönsted and King the velocity was determined at 15° with 0.0100 N sodium hydroxide solution and k was found to be 0.00442. Multiplying Brönsted and King's velocity constant by 2.30 one obtains 0.00437. From this it is evident that the experimental method gives results in fair agreement with the results of the authors mentioned.

The Temperature Coefficient

The rate of reaction with 0.01 N sodium hydroxide solution at 80° is too rapid for accurate measurement. In order to obtain an accurate value of the temperature coefficient over the range 20–80°, and to eliminate the error in the standardization of the less concentrated sodium hydroxide solutions, a modification of the "two-thermostat" method[7] was used. A carbonate-free solution of sodium hydroxide was siphoned into four flasks, two of which were placed in each bath. When the solutions had reached the temperatures of the baths, equal weights of nitrosotriacetoneamine were added and the reaction was followed in the usual way. By this means the solutions were made strictly comparable.

Table II gives the temperature coefficients and the corresponding values of Q from the Arrhenius equation, $d\,ln\,k/dt = Q/RT^2$. From the average value of Q, 16,400, the velocities are calculated for the various temperatures by taking the values of the constant k at 30° from Table I. The observed values are given for comparison.

TABLE II

TEMPERATURE COEFFICIENTS

Temp. coeff.	Q	k_{obs} for 0.0100 NaOH	T, °C.	$k_{\text{calcd.}}$
$k_{30}/k_{20} = 2.57$	16,700	0.00442	15	0.00441
$k_{40}/k_{30} = 2.42$	16,700	.00708	20	.00717
		.0182	30	....
$k_{60}/k_{40} = 4.75$	16,100	.0440	40	.0436
		k_{obs} for *0.00200 NaOH*		
		0.00384	30	.....
$k_{80}/k_{60} = 4.02$	16,200	.0441	60	.0452
		.175	80	.184

Discussion and Study of "Primary Salt Effect"

According to Brönsted's theory[8] a reaction like the decomposition of nitrosotriacetoneamine comes under the general case A° (non-electrolyte) + OH $\longrightarrow$ $A(OH)^-$ (the critical complex), where the velocity of the reaction is expressed by the equation $v = k[A^\circ][OH^-]f_{A^\circ}f_{OH^-}/f_{A(OH)^-}$. Since the activity coefficients are dependent on the ionic type, f_0f_1/f_1 becomes f_0 and we have[9] $v = k[A^\circ][OH^-]f_0$. Brönsted calls the change in f_0 upon addition of salt "primary salt effect." Generally speaking, f_0 increases from 2 to 4% when the total salt concentration increases from 0.02 N to 0.1 N. The effect is linear. For this particular reaction Brönsted finds $100k = 0.192 - 0.13c$, where c is the total equivalent salt concentration. From this the effect amounts to about 7% in 0.1 N salt solution.

Two questions seem to be worth considering: (1) is the magnitude of the primary salt effect the same when the concentrations of the nitroso-

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[7] Rice and Kilpatrick, THIS JOURNAL, **45**, 1409 (1923).

[8] (a) Brönsted, *Z. physik. Chem.*, **102**, 169 (1922). (b) Brönsted and Teeter, *J. Phys. Chem.*, **28**, 579 (1924).

[9] More recently Bronsted has introduced an additional term depending on the medium [*Z. physik. Chem.*, **115**, 337 (1925)].

amine and salt are kept constant and the hydroxyl-ion concentration is altered? (2) for identical concentrations of reactants is the magnitude of the salt effect the same at two temperatures?

A method of testing the effect of temperature on primary salt effect at once suggested itself. If the primary salt effect is appreciably different at different temperatures, the temperature coefficient of the reaction should change with addition of salt. This has already been tested in the case of hydrogen-ion catalysis by Rice and Lemkin.[10] They found that although the addition of neutral salt increased the velocity as much as 50%, there was no alteration in the temperature coefficient for the reaction between acetone and iodine, catalyzed by strong monobasic acids. It is true that their temperature range was small, but the accuracy of the method enabled detection of very small differences. No work of this kind has been done for hydroxyl-ion catalysis, and although the nitrosoamine reaction does not lend itself to such a careful study it was thought worth while to carry out some experiments along this line.

The method used was essentially the "two-thermostat" method, all solutions being strictly comparable. The results of a number of experiments are shown in Table III.

Table III

Effect of Salt on Temperature Coefficient

Approx. concn nitroso-amine, M	NaOH, N	NaCl, N	Total equiv. salt concn.	k_{40}/k_{30}
0.012	0.01	0.09	0.10	2.38
.012	.01	.09	.10	2.39
.008	.01	.40	.41	2.41
006	.01	1.00	1.01	2.41
With 0.01 N NaOH alone, the average value of k_{40}/k_{30} is				2.42

Experiments were also carried out at 60° and 80°. The average value of k_{80}/k_{60} was 4.02 for 0.002 N sodium hydroxide solution, while the value in the presence of salt was 4.12. Here the results were not as reproducible as with 0.01 N sodium hydroxide at lower temperatures. From the results it is evident that increase in salt concentration causes no appreciable change in the temperature coefficient. Therefore, either the activities of the non-electrolyte and salt change very little with temperature, or there is a compensating effect.

Table IV

Reaction in Glycerol Solution

0.01 N NaOH was used in all experiments

Glycerol, %	k_{40}	k_{30}	k_{40}/k_{30}
0	0.0439	0.0182	2.42
40	.00736	.00294	2.50
40	.00714	.00284	2 51

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[10] Rice and Lemkin, This Journal, 45, 1896 (1923).

In a previous study of hydrogen-ion catalysis it was found that nonelectrolytes do not affect the temperature coefficient in the reaction between acetone and iodine. A few experiments with nitrosotriacetoneamine were carried out in 40% glycerol solution, and the results are recorded in Table IV.

The velocity constants show a decrease of over 80% while the k_{40}/k_{30} remains practically unchanged. In this connection it is interesting to note the results obtained by Corvin[11] on the change in activity of the hydroxyl ion with increasing concentration of glycerol. At 25° for 0.01 N sodium hydroxide solution Corvin gives 0.00883 as the activity of the hydroxyl ion, and for 0.01 N sodium hydroxide solution in 40% glycerol he gives the value 0.00135. The activities of the hydrogen ion are 1.16×10^{-12} and 7.06×10^{-12}, respectively. It would appear that the decrease in the velocity of reaction is of the same order as the decrease in the activity of the catalyst. These values also explain why the addition of glycerol increases the rate of reaction for cases of hydrogen-ion catalysis and decreases it for cases of hydroxyl-ion catalysis.

The effect of sodium chloride on the rate of reaction has been determined for 0.01 N sodium hydroxide solution at 30° and 40°, and for 0.00190 N sodium hydroxide at 60° and 80°. These results can most readily be expressed for dilute solution (up to 0.25 N) by the equations below. For the work at 30° and 40° the concentration of the nitrosotriacetoneamine was 0.008 M, and at 60° and 80° approximately 0.020 M. These concentrations were chosen as being convenient for the experiments in buffer solutions and are approximately those used throughout the rest of the work.

0.0100 N NaOH at 30° $k = 0.0183 - 0.010c$
at 40° $k = .0443 - .024c$
0.00190 N NaOH at 60° $k = .0419 - .024c$
at 80° $k = .166 - .07c$

In answer to Question 1, previously raised, it might be stated that, in general, for the same total salt concentration the salt effect is greater the lower the concentration of the hydroxyl ion. This would explain the difference in the magnitude of the salt effect between my results and those of Francis. Most of his work was done with higher concentrations of alkali. Below 0.002 N sodium hydroxide solution the differences are not detectable, being within the experimental error of the measurements.

"Secondary Kinetic Salt Effect"

This is discussed in detail by Brönsted[3,8b] and a brief review will suffice here. The secondary kinetic salt effect is ascribed to a change in the concentration of one of the reactants upon the shifting of an equilibrium which involves weak electrolytes. For example, if the hydroxyl ion is in equi-

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[11] Corvin, *J. Chem. Soc.*, 127, 2788 (1925).

librium with a weak base, a change in the salt concentration may markedly alter the concentration of the hydroxyl ion and consequently change the reaction rate. The magnitude and direction of the effect depend on the ionic type involved. In the general case, for ideal solutions, where $A + B \rightleftarrows C + OH^-$, the direction of the change in the concentration of the hydroxyl ion with increase in salt concentration depends on whether the sum of the squares of the ionic charges on A and B is greater or less than the sum of the squares of the charges on C and the hydroxyl ion. If greater, the concentration of the hydroxyl ion is decreased; if less, increased. My results with phosphate buffer at 30° and 40° are in agreement with the work of Brönsted at 15° and will not be given here. However, a few of the results at 80° are given. The buffer solution used was 0.05 *M* in potassium dihydrogen phosphate and 0.0468 *M* in sodium hydroxide. Its Sörensen (P_H) value at room temperature was approximately eight. The equilibrium can be expressed by the equation $HPO_4^= + H_2O \rightleftarrows H_2PO_4^- + OH^-$ and K_a (thermodynamic mass-action constant) $= a_{H_2PO_4^-}\ a_{OH^-}/a_{HPO_4^=} = [H_2PO_4^-][OH^-]/[HPO_4^=] . f_1^2/f_2$, where f_1 and f_2 are the activity coefficients. Now the value of the fraction f_1^2/f_2 increases with increasing salt concentration. Consequently, the concentration of the hydroxyl ion decreases. The concentration of the hydroxyl ion can be determined by dividing the velocity constant for the buffer solution by the appropriate velocity constant for the nearest sodium hydroxide concentration and the same salt concentration. The nearest sodium hydroxide concentration is 0.001 and the velocity constant can be calculated from the equation $k = 0.875 - 0.035c$. From the composition of the buffer solution the concentrations of the other ions are readily obtainable and from them the customary mass-action equilibrium constant, K_c, can be calculated. Table V gives the results of the calculation.

TABLE V

DECOMPOSITION OF NITROSOTRIACETONEAMINE IN PHOSPHATE BUFFER SOLUTIONS

KCl	Total equiv. salt concn.	k for buffer	k for 0.001 N NaOH + salt	$OH^- \times 10^5$	$K_c \times 10^{-6}$
0	0.147	0.00280	0.824	3.40	2.33
0	.147	.00282	.824	3.42	2.34
0.031	.178	.00271	.813	3.33	2.28
.067	.214	.00249	.800	3.11	2.13
0	.147	.00281	.824	3.41	2.33
0	.147	.00280	.824	3.40	2.33

K_c decreases with increasing salt concentration. The assumption is made that the magnitude of the primary salt effect is the same for 0.00001 *N* hydroxyl ion as for 0.001 *N*. In his calculations for a different phosphate buffer, Brönsted assumed that the primary salt effect was the same for 0.005 *N* as for 0.01 *N*.

A more rigorous test of the concept of secondary kinetic salt effect was made in glycine-sodium hydroxide mixtures. Here we have $NH_2CH_2COO^- + H_2O \rightleftarrows NH_2CH_2COOH + OH^-$; $K_a = [NH_2CH_2COOH][OH^-]/[NH_2CH_2COO^-].f_0f_1/f_1 = K_cf_0$. Since the change in f_0 is small for small changes in salt concentration, only a small change in the velocity constant would be expected. Experiments were carried out in which the total equivalent salt concentration was changed from 0.05 *N* to 0.5 *N*. The primary salt effect was determined experimentally for 0.5 *N* total salt concentration. The results obtained with a solution 0.05 *N* in glycine and 0.05 *N* in sodium hydroxide are given in Table VI.

TABLE VI

DECOMPOSITION OF NITROSOTRIACETONEAMINE IN GLYCINE BUFFER SOLUTIONS

T, °C.	NaCl	Total equiv. salt concn.	*k* for buffer	*k* for 0.01 *N* NaOH + salt	OH^- concn.	$K_c \times 10^{-4}$
30	0	0.05	0.00342	0.0178	0.00192	0.749
30	0 45	.50	.00357	.0150	.00238	1.19
40	0	.05	.00826	.00430	.00192	0.749
40	0.45	.50	.00831	.00362	.00230	1.11
60	0	.05	.0423	.225	.00188	0.735
60	0.45	.50	.0419	.169	.00248	1.30

An examination of Table VI brings out the following points: (1) the secondary salt effect is as predicted; (2) the velocity constants are not greatly changed by change in salt concentration. The explanation of the second fact becomes apparent on consideration of primary and secondary salt action. As f_0 decreases the activity of the non-electrolyte decreases and the velocity would be expected to decrease. On the other hand, K_c increases, the hydroxyl-ion concentration increases, and the velocity would be expected to increase. Thus we have two compensating effects. It is possible that primary and secondary salt action are not essentially different in mechanism.

The temperature coefficient, k_{40}/k_{30}, was determined by the "two-thermostat" method and found to be 2.36 with the glycine-sodium hydroxide buffer when no salt was added, and 2.34 when 0.45 *N* in sodium chloride.

With the borate-sodium hydroxide buffer it is not feasible to calculate K_c in the usual way, as it is difficult to say what ions are involved. Table VII shows the change in the velocity constant with increasing salt concentration. The buffer solution used was 0.05 *M* in boric acid and 0.021 *N* in sodium hydroxide. Its Sörensen value was approximately nine. The experiments were carried out at 80°

TABLE VII

DECOMPOSITION OF NITROSOTRIACETONEAMINE IN BORATE BUFFER SOLUTIONS

NaCl	0	0	0.11	0.18	0.57	0.68
k	0.0191	0.0187	.0177	.0166	.0124	.0108

With increasing salt concentration the velocity decreases.

Incidentally, having determined the primary salt effect, the decomposition of nitrosotriacetoneamine is readily adaptable to the estimation of Sörensen values between seven and ten at temperatures above 60°.

The author is indebted to Professor F. O. Rice for his kindly criticism.

Summary

1. The catalytic decomposition of nitrosotriacetoneamine has been studied in solutions of sodium hydroxide and in alkaline buffer solutions.

2. The rates of reaction and the temperature coefficients have been determined from 20° to 80°.

3. The temperature coefficient is unaffected by neutral salt.

4. The results are in agreement with Brönsted's concept of secondary kinetic salt effect.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT OF THE JOHNS HOPKINS UNIVERSITY]

THE CATALYTIC ACTIVITY OF DUST PARTICLES

BY F. O. RICE

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When a chemical reaction proceeds in a closed vessel it is subject to two influences which can ordinarily be neglected but which in some reactions completely determine the speed, because in the absence of the particular influence the reaction will not take place at a measurable rate. The first of these influences is the surface of the containing vessel; if, as is commonly the case, this is of glass, the reaction is surrounded by a thin envelope of condensed water containing many dissolved substances the most important of which is probably the hydroxyl ion. This film catalyzes many reactions between liquids, between dissolved substances and between gases; examples such as the interconversion of liquid keto-enol isomers,[1] the change of *n*-nitrocamphor to the pseudo form in different solvents[2] and the bromination of ethylene[3] illustrate the important chemical effects of this surface film, since none of these reactions takes place in a vessel with non-reactive walls.

The second influence arises from the presence of finely-divided dust particles which are always present unless special precautions are taken to exclude them. If an intense beam of light be passed through air or other gas and viewed at right angles against a dark background, the path of the beam is plainly visible owing to light scattering by the great numbers of

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[1] Meyer and Schoeller, *Ber.*, **53**, 1410 (1920). Meyer and Hopff, *Ber.*, **54**, 579 (1921).

[2] Lowry, *J. Chem. Soc.*, (a) **75**, 220 (1899); (b) **83**, 1316 (1903).

[3] Stewart and Edlund, THIS JOURNAL, **45**, 1014 (1923). Norrish, *J. Chem. Soc.*, **123**, 3006 (1923).

motes present; if a vessel of water or other liquid be held in the path of the beam, considerable scattering also takes place showing the presence of dust which is not removed even by careful distillation. Since distilled water contains about 25,000 suspended particles per cc.,[4] all of our chemical reactions occur in the presence of considerable amounts of suspended dust and it appeared not unlikely that these particles exert a catalytic influence which would explain a number of anomalous results in supposedly homogeneous reactions.

great number of studies have been made of systems[5] containing suspended dust particles, but almost without exception the work has been confined to light-scattering experiments and to the technique of dust removal; practically nothing has been done from the chemical point of view, probably because certain abnormal chemical phenomena that are due to dust have come into prominence only in comparatively recent years.

It soon became evident, however, that there are many reactions ordinarily considered homogeneous that are really catalyzed by solid surfaces and three representative reactions, namely, the thermal decomposition of hydrogen peroxide, the oxidation of sodium sulfite and the oxidation of benzaldehyde are now being investigated in this Laboratory. The thermal decomposition of hydrogen peroxide is an example of a reaction that is to some extent catalyzed by the walls of the vessel but mainly by suspended dust particles; when hydrogen peroxide, free from dust, is kept in a vessel of fused silica it is a remarkably stable substance and may be heated for several days to 60° without appreciable decomposition. There does not seem to be any evidence of a homogeneous decomposition, for when a solution of hydrogen peroxide free from preservative and organic matter is heated, the decomposition is a zero-order reaction, the rate being independent of the concentration of the hydrogen peroxide. The results of previous workers indicating a unimolecular reaction are due to the gradual destruction of solid organic matter in the solution.

The oxidation of sodium sulfite is almost entirely a dust reaction, since experiment shows that a dust-free alkaline solution of sodium sulfite may be left almost indefinitely in contact with dust-free oxygen without undergoing oxidation. The remarkable nature of this reaction may be gaged from an experiment in which we passed a dust-free mixture of sulfur dioxide and oxygen into a vessel, one bulb of which contained ordinary distilled water and the other bulb dust-free water; after 24 hours the former bulb gave a distinct test for sulfate but no sulfate was found in the clean bulb. The oxidation of benzaldehyde, on the other hand, is a wall reaction and the presence or absence of dust has a negligible effect.

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[4] Kenrick, *J. Phys. Chem.*, **26**, 72 (1922).

[5] A fairly complete bibliography is given by Martin, *Trans. Roy. Soc. Canada.*, **16**, 276 (1922).

It also seems likely that the anomalous results obtained in some photochemical reactions are to be ascribed to the presence of dust. Einstein's law of the photochemical equivalent fails for many of these reactions, one quantum of light of the characteristic frequency causing from 1 to 1,000,000 molecules to react. One of these reactions, namely, the photochemical decomposition of hydrogen peroxide, much more nearly obeys the law when suspended dust particles and inhibitors are removed from the solution; quantitative measurements are now in progress to test whether the law is followed exactly. It is evident, therefore, that the photochemical decomposition takes place on the surface of the dust and that the hydrogen peroxide is adsorbed in aggregates, the average size of these being given by some multiple of the quantum yield of the reaction. We may regard one of the molecules on the surface as absorbing a quantum of light, decomposing and the action then spreading throughout the whole adsorbed aggregate. We might expect the quantum yield on this basis to diminish with dilution because the amount of substrate adsorbed will also diminish with dilution; furthermore, only reactions that occur with liberation of free energy should give these large deviations from the equivalence law. All these conclusions are in accord with the results of photochemical investigations.

Several studies of the work described in this introduction have now been completed and the results will be published shortly; the work is being extended to other reactions, particularly those in the gaseous state, but it has not yet been determined whether dust is an appreciable factor in this type of reaction. An interesting field lies in the investigation of the character of catalyst surfaces; if some dust-free water be prepared by Martin's method[6] and the bulb containing the clean water be shaken violently, the water will be found to contain large numbers of motes detached from the surface of the vessel; the vessel may be filled again with clean water and the process repeated almost indefinitely.[7] We are now conducting these experiments using a platinum catalyst and comparing the catalytic activity of the old and the new surface as well as the catalytic activity of the platinum particles detached from the surface; similar experiments are in progress using a poisoned catalyst. Our results indicate that solid surfaces consist of loose, porous and scaly layers that are easily rubbed off; a freshly melted surface does not, however, behave in this manner, and only after more violent and long continued shaking does it yield any quantity of motes.

Some of the results obtained so far in this work, especially those dealing with photochemical decompositions, are only semi-quantitative and neces-

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[6] Martin, *J. Phys. Chem.*, **24**, 478 (1920).

[7] This has already been observed by Kenrick, Gilbert and Wismer, *ibid.*, **28**, 1305 (1924).

sarily, also, part of the discussion is somewhat speculative in character. However, it seems desirable to publish this preliminary paper because the work which has been in progress for the past two years has yielded results proving beyond doubt that suspended dust is an important factor in three reactions and may be the cause of anomalous results in a great many others.

Negative Catalysis

When a reaction is catalyzed by a weak acid, the addition of one of its salts lowers the velocity; similarly, a number of reactions occurring in absolute alcohol, such as the esterification of acids,[8] the formation of a lactone from an hydroxy acid,[9] the alcoholysis of amides,[10] etc., are very sensitive to the addition of small quantities of water, the reaction rate being greatly diminished in all cases; reactions that occur in 100% sulfuric acid, such as the decomposition of oxalic acid,[11] are also diminished in velocity by the addition of small quantities of water. All these are homogeneous reactions in which the negative catalyst such as the neutral salt or the water acts probably by diminishing the concentration of the hydrogen-ion catalyst. There is a second type of negative catalysis which consists of the inhibition of chemical reactions by minute traces of foreign substances. The oxidation of benzaldehyde is typical of a whole host of reactive organic substances which undergo slow oxidation in the presence of air, and reaction is inhibited or accelerated by minute traces of different substances; other examples are the decomposition of hydrogen peroxide and the oxidation of sodium sulfite.

It is convenient at this point to review briefly the subject of negative catalysis, noting that up to the present no attempt has been made to draw any distinction between the two types. The Luther-Titoff conception[12] of negative catalysis postulates that the phenomenon cannot occur in a reaction which is entirely free from positive catalysts, being due entirely to the destruction or inhibition of these by the negative catalyst. Recently Taylor[13] has criticized this view and advanced the hypothesis that the inhibitor combines with one of the reactants to form a double compound which subsequently dissociates, regenerating the inhibitor and reactant; the inhibitor is therefore a competitor for one of the reactants and owing to the probably high rate of double compound formation,[14] it is as-

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[8] Goldschmidt, *Z. Elektrochem.*, **15**, 4 (1909).

[9] Kailan and Neumann, *Z. physik. Chem.*, **101**, 63 (1922).

[10] Reid, *Am. Chem. J.*, **41**, 483 (1909).

[11] Bredig and Lichty, *J. Phys. Chem.*, **11**, 255 (1907).

[12] Luther, *Z. physik. Chem.*, **45**, 662 (1903). Titoff, *ibid.*, **45**, 641 (1903).

[13] Taylor, *J. Phys. Chem.*, **27**, 322 (1923).

[14] The rate of collision of two gases may be calculated on the basis of ordinary kinetic considerations; assuming that in such a mixture of two gases every collision results in chemical combination, a velocity constant $k = 10^{15}$ is obtained; this would be an upper limit for the rate of double compound formation.

sumed that one molecule of inhibitor is able to prevent many molecules from reacting. This hypothesis is supported by some recent work[15] in which it was shown that double compound formation and inhibitory power are related. A third hypothesis to explain catalysis has been advanced by Christiansen[16] who assumes that negative catalysis is really due to the presence of chain reactions; when two reacting molecules combine, the resulting "hot" molecule is supposed to be able, on the first collision, to activate a molecule of reactant which combines forming a second hot molecule, thus starting a chain reaction in the system. The rate of such a reaction is proportional to the number of chains starting per minute multiplied by the average length of the chain; the action of the inhibitor is explained by assuming that it breaks the chains, the energy of the hot molecules being dissipated on collision with an inhibitor. This concludes the review of the previous work.

We may now consider the second type of negative catalysis and, in particular, certain peculiarities that are common to these reactions. They are extremely sensitive to the most minute traces of impurities which may either accelerate or retard the reaction; a wide variety of substances, especially organic compounds, retard the reactions; finally, there seems to be something erratic connected with the phenomenon which makes duplication of results impossible in spite of most careful work. Comments on this erratic character of the results appear in many of the publications in this field, the following comment being a translation from a paper[17] by Moureau and Dufraisse on the oxidation of benzaldehyde.

> In the course of these studies, we have occasionally noted strange, capricious and even anomalous effects. Thus, we have noticed that the retarding of the oxidation, at first quite sharp, suddenly stopped. Furthermore, after a sort of incubation, there is sometimes an inversion of the phenomenon, the oxidation being accelerated and not retarded. We can only call attention to the facts here, but the conditions underlying the results remain to be determined.

The three experimental observations just recorded provided the clue that the phenomenon is really heterogeneous catalysis, the catalyst being suspended dust,[18] its action being promoted or poisoned by minute traces of foreign substances—a behavior very common among heterogeneous catalysts; the erratic nature of the phenomenon also becomes quite clear.

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[15] Underwood, *Proc. Nat. Acad. Sci.*, **2**, 78 (1925).

[16] Christiansen, *J. Phys. Chem.*, **28**, 145 (1924).

[17] Moureau and Dufraisse, *Compt. rend.*, **175**, 127 (1922). This is one of a series of papers published in *Compt. rend.* for 1922–1925. ("Au cours........préciser.")

[18] Certain of these reactions such as the benzaldehyde oxidation are catalyzed mainly by the walls of the vessel and only to a minor extent by dust particles. The oxidation of benzaldehyde will not be dealt with further in this paper, because Dr. Reiff, working in this Laboratory, has now completed a study of it which will be published shortly.

Thermal Decomposition of Hydrogen Peroxide.[19]—Most of the investigations in this connection deal not with the rate in pure aqueous solution but with the effect of acids, alkalies, metals and conserving agents on the stability. In two recent papers,[20] however, the thermal decomposition has been extensively studied. Most of the workers agree that the reaction is unimolecular but the constants obtained show the widest variations. Lemoine considers that the surface of the containing vessel is an important factor in determining the rate, whereas Clayton considers that colloidal organic matter is of primary importance. Both of these workers used peroxide containing inhibitor, since both observed "une certaine inertie au début" and this is a phenomenon which we find does not occur when pure hydrogen peroxide is used. It does not seem worth while to discuss this work further, because the results were obtained in presence of an unknown inhibitor at an unknown concentration; indeed we find that by a proper selection of the nature and concentration of an inhibitor the reaction rate may be varied over an extremely wide range and the concentration-time curve can assume a great variety of shapes.

It seems desirable at this point to discuss the application of the term "unimolecular" to this change since, as has been previously pointed out,[21] "unimolecular" is commonly used when "pseudo-unimolecular" is meant. At ordinary temperatures it is not possible for any unimolecular thermal decomposition of hydrogen peroxide to occur because this would mean the production of a molecule of water and an atom of oxygen, a reaction which *absorbs* about 50,000 calories of free energy; the reaction could be dimolecular but there is no evidence for this in any published work. Actually, we find that the decomposition of hydrogen peroxide prepared by ourselves and kept quite free from any preservative is a zero-order reaction which is, of course, characteristic of reactions at solid surfaces. The active surface in this case is mainly suspended dust particles because when these are removed by Martin's method[6] the rate of decomposition falls enormously. The remaining slow rate is due mainly to catalysis by the walls of the vessel; this effect may be almost entirely removed by collecting the dust-free peroxide in a freshly fused quartz or Pyrex vessel. We have found empirically that a freshly fused glass surface is comparatively inactive, whereas glass which has been "roughened" by some such treatment as immersing in hot cleaning solution is very active catalytically. Material prepared in this way is extremely stable, far more so than commercial samples, even those heavily loaded with preservative; it is quite

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[19] The experiments described in this section were made in collaboration with Dr. O. M. Reiff; a full account of this work will be published shortly.

[20] Lemoine, *J. chim. phys.*, **12**, 1 (1914). Clayton, *Trans. Faraday Soc.*, **11**, 164 (1915). See also Spring, *Z. anorg. Chem.*, **10**, 161 (1895).

[21] "Treatise on Physical Chemistry," Ed. by Taylor, Van Nostrand Co., New York, 1925, vol. 2, p. 874 (1924).

simple by this method to prepare a sample of say 50% aqueous hydrogen peroxide which has a half life of several months at 60°; the best sample prepared by Clayton using peroxide *containing inhibitor* had a half life of about five days. The whole of this work leads to the conclusion that the ordinary thermal decomposition of hydrogen peroxide is a heterogeneous reaction taking place mainly on the surface of suspended dust particles, that the action of inhibitors is to poison the active surface of the dust, and finally that the ordinary thermal decomposition in the presence of preservatives consists first of oxidation and destruction of the adsorbed inhibitor, which corresponds to the initial inhibition usually observed, and second of a competition between the hydrogen peroxide and dissolved inhibitor for the active surface of the dust; this second reaction in some cases gives a curve very approximately resembling that of a first-order reaction.

Thermal Oxidation of Sodium Sulfite.—The early studies of Bigelow[22] and Young[23] showed that this reaction is a typical example of negative catalysis of the second kind, the reaction being inhibited sometimes to an extraordinary degree by traces of organic compounds. It seemed possible that these experiments, as well as those of Titoff,[12] could be readily explained by catalysis due to suspended dust; thus Titoff's experiments with copper sulfate and mannitol indicate that he was simply copper plating the dust particles and then poisoning the copper with mannitol. The reaction is usually considered to be unimolecular with respect to the sodium sulfite[24] but here again we meet the same difficulty as in the decomposition of hydrogen peroxide, that such a process requires the production of atomic oxygen and therefore cannot occur; it appears that the oxidation of sodium sulfite must be either dimolecular with respect to the sulfite or a heterogeneous reaction like the decomposition of hydrogen peroxide. Our experiments show that the oxidation of sodium sulfite is almost entirely a dust reaction, the walls of the vessel having a negligible effect. Using Spring's method,[25] the dust was removed by envelopment by a gelatinous precipitate, the resulting solution of sodium sulfite being optically clear and giving no absorption of oxygen over a period of several hours; if this clear solution is poured into a beaker and then poured back into the apparatus, the resulting solution contains great numbers of motes and oxidizes at a rapid rate. It may easily be shown that copper alone has no catalytic activity because the sulfite solution may be freed from dust by precipitating in it copper hydroxide; the resulting clean solution does not oxidize in the presence of oxygen. The

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[22] Bigelow, *Z. physik. Chem.*, **26**, 493 (1898).

[23] Young, THIS JOURNAL, **24**, 297 (1902).

[24] See Mack, Osterhof and Kraner, *ibid.*, **45**, 617 (1923).

[25] Spring, *Rec. trav. chim. Pays-Bas.*, **18**, 153 (1899).

experimental part of this work, done in collaboration with Mr. George I. Lavin, is still in progress and will be reported in a later communication.

Photochemical Reactions

From the results obtained with thermal reactions it appeared extremely likely that the abnormalities of photochemical reactions are in part at least due to suspended dust, and two reactions, the photochemical decomposition of hydrogen peroxide and the combination of hydrogen and chlorine, are now under investigation in this Laboratory; this work is in collaboration with Mrs. M. L. Kilpatrick but only some preliminary results with reference to the hydrogen peroxide decomposition are now available. Both these reactions show large deviations[26] from Einstein's photochemical law, one quantum of light in the case of a 2% hydrogen peroxide solution decomposing about 80 molecules. The effect of dust on this reaction may be illustrated in a striking manner by a qualitative experiment; two quartz flasks are placed equidistant from a mercury lamp and protected from heat rays by a water screen. A 2% solution of peroxide is then made up and part is poured into one flask and the remainder is placed in the second flask and freed from dust by Martin's method;[6] when the flasks are near the lamp the first flask shows a rapid evolution of gas so that the solution appears to be boiling vigorously whereas the second flask shows a very slow and hardly perceptible gas evolution. Many experiments such as this have been performed in which the rate of decomposition of the peroxide has been followed both by gas evolution and by titration, and there is no doubt that the presence of dust is the main factor in the ordinary photochemical decomposition of peroxide. When a dust-free solution of peroxide, which a test shows to decompose extremely slowly, is poured out of the flask into a beaker and then back to the flask, the rate of decomposition greatly increases, attaining practically the same value as the blank which had not been freed from dust; in the process of pouring a dust-free liquid from one vessel to another in laboratory air, it acquires practically the same dust content as untreated liquid. Owing to the great ease with which a clean liquid picks up dust, a special technique has to be followed in handling and preserving such liquids in a dust-free condition; the ordinary chemical method of cleaning a vessel by hot dichromate solution has no effect so far as the dust is concerned because on pouring out the cleaning solution, the vessel becomes filled with ordinary air and the washing with distilled water completes the process of re-introducing the motes; indeed, by roughening the glass surface, the dichromate works mischief in two ways, first by making it easy to detach motes from the surface by shaking the vessel and second by increasing any catalytic activity which the surface may have had originally.

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[26] See Ref. 21, Chap. 18.

We find that the rate of decomposition of hydrogen peroxide by ultraviolet light is roughly proportional to the dust content as measured by the light-scattering power of the solution and it remains, therefore, to find whether the dust-free solution obeys the photochemical equivalent law. The measurements are difficult because low-voltage arcs do not decompose hydrogen peroxide at a rate convenient for measurement. If the dust-free material obeys the law, its rate of decomposition will be only about 1% of the ordinary rate;[27] it requires about 90 minutes' exposure to a mercury-vapor lamp to obtain a quantitative measurement on an ordinary dusty solution, so that we may expect that a dust-free solution would require a week's exposure both day and night to give sufficient decomposition. The reaction is now being investigated, using a high-tension spark as source of light with a monochromator and standard thermopile.

It is evident, therefore, that dust may act as a photocatalyst and is perhaps the only one; substances which change the rate of a photochemical reaction act by promoting or poisoning the catalytic activity of the dust. The term photocatalyst as ordinarily used is therefore applied to substances which promote the action of the dust, probably by bringing about increased adsorption, whereas negative photocatalysts poison the dust, probably by being adsorbed themselves instead of the substrate. If this is true it is evident that an inhibitor must be placed in the solution, since its use in a separate solution as a screen can only bring about absorption of the active radiation. Anderson and Taylor have shown[28] that the same substance is much more effective as an inhibitor when added directly to the solution than when used in a separate solution as a screen. It is, of course, possible for a substance not adsorbed by the dust to act as an inhibitor merely by absorbing the active radiation.

On the basis of these views it may be no longer necessary to postulate the existence of reaction chains[29] as a mechanism for photochemical changes in which the quantum yield is very high; the substrate is supposed to be adsorbed on the surface of the dust and on the walls of the vessel, in isolated aggregates, the average size of which is given by a multiple of the quantum yield of the reaction; one quantum of light of characteristic frequency is absorbed by one of the molecules which decomposes and the action spreads throughout the whole aggregate. In order for such a process to occur it is obvious that the free energy of the system must diminish, and on this basis the heat change of the reaction is not important since it is conceivable that an endothermic reaction could give a high quantum yield. Some such

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[27] See Henri and Wurmser, *Compt. rend.*, **151**, 1040 (1910). Kornfeld, *Z. wiss. Phot.*, **21**, 66 (1921).

[28] Anderson and Taylor, THIS JOURNAL, **45**, 650, 1210 (1923).

[29] In the discussion of photochemical reactions that follows, individual references to the various points will not be given because two very recent reviews are now available. See *Trans. Faraday Soc.*, **21**, 438 (1926); *Ann. Repts. Progress Chem.*, **22**, 333 (1925).

explanation as this appears to be very likely for the hydrogen peroxide decomposition and may apply to other photochemical changes of high quantum yield.

The results now obtained in this work provide additional confirmation of Taylor's concept[30] of a catalytic surface in which the Langmuir active areas are shown to occupy only a small fraction of the surface; the quantum yield of a reaction enables us to measure the average number of molecules adsorbed by these active centers and suggests several lines of investigation that are now in progress; it is possible to free a system from dust and then introduce various materials in the form of dust and measure the quantum yield in each case; the effects of poisons, temperature and dilution are also being investigated. In this connection it is interesting to consider the temperature coefficients of photochemical processes because the change in rate with temperature will depend, for those reactions of high quantum yield, upon the change of adsorption of the substrate with temperature; since the heat of adsorption is in general positive, the effect of rise in temperature will be to diminish the size of the cluster of molecules at an active point on a dust particle, which would have the effect of causing abnormally low or negative temperature coefficients for photochemical reactions of high quantum yield; doubtless the conflicting results obtained in these measurements are due to differences in composition of active suspended material.

It is evident that photosensitization processes may occur with large quantum yields, if an excited atom or molecule collides with aggregates adsorbed on the surface of the dust, and this explanation is suggested for such experiments as those of Bonhoeffer[31] on the decomposition of ozone using bromine as sensitizer; 30 molecules of ozone are decomposed for each quantum of energy absorbed and no completely satisfactory mechanism for such an abnormal yield has yet been found.

The existence of induction periods in photochemical reactions is doubtless related, as in thermal reactions, to the presence of adsorbed materials either on the walls of the vessel or on the dust particles; in a recent paper Norrish[32] has shown that ammonia poisons the surface of the vessel in the hydrogen-chlorine combination but he did not examine for the effect of suspended dust. On the basis of the views put forward in this paper the hydrogen-chlorine reaction provides an extraordinary example of the variation in size of these adsorbed aggregates since the number of molecules of hydrochloric acid formed per light quantum varies from 1,000,000 when the reaction occurs at ordinary pressures to 20 when the reaction occurs at 0.01 mm.[33] It seems desirable, therefore, to discuss the mech-

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[30] Taylor, *Proc. Roy. Soc.*, **108A**, 105 (1925).

[31] Bonhoeffer, *Z. Physik*, **106**, 403 (1923).

[32] Norrish, *J. Chem. Soc.*, **127**, 2316 (1925).

[33] Marshall, *J. Phys. Chem.*, **29**, 1453 (1925).

anism of such reactions because it must be quite different from those discussed by Born and Franck[34] and by Franck.[35] When a quantum of light strikes an adsorbed aggregate of chlorine molecules or hydrogen peroxide molecules, it is absorbed by one of them with consequent excitation; since the excited molecule is in combination with the rest of the aggregate, the reaction can pass throughout the adsorbed mass *via* either molecular bonds or the surface of the dust particle. If we imagine ten quanta of absorbable light entering a solution of hydrogen peroxide, nine of them may collide with molecules in solution whereas the tenth may collide with a molecule attached to an aggregate on a dust particle and thus decompose the whole aggregate; for practical purposes we may therefore regard the size of the aggregate as being some multiple of the quantum yield. For hydrogen peroxide the multiple is probably very small because the scattering power of the dust is probably comparable with the absorptive power of the peroxide. An important point comes up in this connection because the absorption spectrum of the adsorbed material may not be the same as when it is in solution; the effect of double-compound formation is in general to move the absorption spectrum towards the longer wave length so that it may be possible to decompose a substance by light which it does not absorb in the homogeneous condition. It appears probable also that the degree of excitation required is less for an adsorbed molecule than for one in the free state because Coehn and Jung[36] showed that after intensive drying of a hydrogen-chlorine mixture (which would destroy the activity of the surface) it reacts only to ultraviolet light and not to blue light which affects the ordinary moist gases. An experiment is now in progress to test the reactivity of the dust-free gases to visible light.

Gas Reactions

Owing to the contradictory results obtained in the studies of some of these reactions it seems desirable to test whether the anomalies are to be ascribed wholly or in part to suspended dust; not only does there seem to be no work in which precautions were taken to remove the dust, but the usual technique of drying the gases with phosphorus pentoxide just before entering the decomposition chamber ensures a great plenitude of suspended particles.[37] Two gas reactions are now under investigation in this Laboratory, namely, the thermal decomposition of ozone and the thermal decomposition of nitrogen pentoxide; although results are not yet available

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[34] Born and Franck, *Z. Physik*, 31, 411 (1925).

[35] Franck, *Trans. Faraday Soc.*, 21, 536 (1926).

[36] Coehn and Jung, *Ber.*, 56, 696 (1923).

[37] See Hartung, *J. Chem. Soc.*, 127, 2697 (1925). In his study with the microbalance the author notes that "the presence of phosphorus pentoxide has been found to be most objectionable because of the fine dust which arises from it with changes of pressure."

it seems desirable to give a preliminary discussion of these reactions. Published results show that many gas reactions occur partly on the wall of the containing vessel and it is certainly reasonable to infer that the supposed homogeneous part of the reaction occurs on the surface of suspended particles. There is conflict of opinion in the case of the thermal decomposition of ozone, Chapman and Clarke[38] believing that the reaction is practically entirely homogeneous whereas Perman and Greaves[39] consider that the reaction occurs mainly on the surface of the vessel. In a very recent paper Griffith and McKeown state:[40] "We are unable from the results of the present work or from the results of previous workers to arrive at a definite conclusion on this point. All that may safely be inferred is that some part at least of the measured rate is due to a heterogeneous change." The decomposition of chlorine monoxide[41] is usually accepted as a homogeneous dimolecular change but the concentration-time curves show a period of inhibition and closely resemble the curves obtained for the decomposition of aqueous hydrogen peroxide, a typical dust reaction. Several other examples of such anomalous results might be quoted, which seems to indicate that until gas reactions have been investigated in the dust-free condition we cannot afford to neglect the possibility that there are no real examples of homogeneous uncatalyzed gas reactions.

We may now consider the most interesting of all the gas reactions, namely the decomposition of nitrogen pentoxide. The generally accepted view[42] is that "there seems to be no reason for doubting the unimolecular homogeneous character of this reaction," although one may well demur in view of the difficulty of finding a reasonably satisfactory theoretical treatment, as well as the unexplained result of Daniels, Wulf and Karrer.[43] It appeared possible that the decomposition was of the usual pseudo-unimolecular type, suspended dust being the catalyst, especially as the technique used by Daniels, Wulf and Karrer would probably free the gases from dust; however, preliminary experiments in collaboration with Miss D. Getz indicate that the rate of decomposition is not affected by dust; the work is still in progress because the experiments are not quite conclusive, in that our filters would not remove very fine dust. Also, there are other hypotheses that it is desirable to test, in particular, that the reaction is due to the presence of a small amount of catalyst. Lowry[44] suggested some time ago that all reactions are catalytic in character although presumably he had in mind that all *slow* reactions are catalytic since, as pointed

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[38] Clarke and Chapman, *J. Chem. Soc.*, **93**, 1638 (1908).

[39] Perman and Greaves, *Proc. Roy. Soc.*, **80A**, 353 (1908).

[40] Griffith and McKeown, *J. Chem. Soc.*, **127**, 2086 (1925).

[41] Hinshelwood and Prichard, *ibid.*, **123**, 2730 (1923).

[42] *Ann. Repts. Progress Chem.*, **22**, 16 (1925).

[43] Daniels, Wulf and Karrer, THIS JOURNAL, **44**, 2402 (1922).

[44] Lowry, *Trans. Faraday Soc.*, **17**, 596 (1922).

out by Perrin,[45] the former suggestion leads to an obvious absurdity. The problem is then to find whether nitrogen pentoxide is likely to contain any small amount of impurity present in constant amount. One of these impurities is nitric acid as may be seen from the following considerations: the nitrogen pentoxide before entering the reaction chamber passes over phosphorus pentoxide, so that we have the following equilibrium: $2HNO_3 + P_2O_5 \rightleftarrows N_2O_5 + 2HPO_3$. The heat of this reaction for gaseous nitric acid and gaseous nitrogen pentoxide is approximately 13,800 cal.; the equilibrium concentration of the nitric acid will not, therefore, vary very much, since the phosphorus pentoxide is used at ordinary laboratory temperatures. Experiments are in progress to test this by drying with the phosphorus pentoxide at different temperatures which also would indicate the presence of any other catalytic impurity introduced in constant amount *via* the drying agent.

Other Reactions

Periodic reactions have been the subject of several extensive investigations recently. Among other reactions, Hedges and Myers[46] investigated the periodic decomposition of hydrogen peroxide by metals, metallic oxides and other substances; Firth and Watson[47] found that with sugar charcoal at higher temperatures the decomposition is periodic. None of these workers, however, state the source of their hydrogen peroxide although this is far more important than the particular substance used to decompose the peroxide; some commercial samples when merely diluted with distilled water give a periodic decomposition curve but we find that the periodicity is due to traces of inhibitor, because the phenomenon is not observed with pure hydrogen peroxide. The periodic reaction observed by Bray[48] also is due apparently to the presence of dust; by varying the amount of dust and inhibitors present in the reaction its periodic character can be increased or suppressed at will. The phenomenon of periodicity appears to be due to a competition between the substrate and an inhibitor for the surface of the vessel, suspended dust or an added solid substance.

Induced reactions probably in some cases at least are examples of heterogeneous catalysis taking place on dust particles. Thus a solution of sodium arsenite alone does not oxidize[49] in air or oxygen but does so in the presence of sodium sulfite, this reaction being typical of a great number of others.[50]

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[45] Perrin, *Trans. Faraday Soc.*, **17**, 605 (1922).

[46] Hedges and Myers, *J. Chem. Soc.*, (a) **125**, 604, 1282 (1924); (b) **127**, 445, 1013 (1925).

[47] Firth and Watson, *ibid.*, **123**, 1750 (1923).

[48] Bray, THIS JOURNAL, **43**, 1262 (1921).

[49] Jorissen, *Z. physik. Chem.*, **23**, 667 (1897).

[50] Shilow, *ibid.*, **42**, 641 (1903). Luther, *ibid.*, **46**, 777 (1903). Jorissen and van den Pol, *Rec. trav. chim.*, **43**, 582 (1924).

It seems likely that the oxidation of sodium arsenite also takes place on the dust which is activated, so far as the arsenite oxidation is concerned, by the sodium sulfite; it is interesting to note in this connection that Chapin[51] found that arsenite could be oxidized easily by oxygen when finely-divided carbon is used as a catalyst.

The possibility that dust is a factor in change of state was suggested by Baker's work on the boiling points of highly dried liquids, in particular by his remarkable observations[52] that dried benzene, b. p. 106°, may be poured onto water and the water boiled through it without the benzene undergoing change; the benzene regains its normal boiling point only after several days' contact with the water. This experiment suggests that the dust and not the water is the actual catalyst and that the drying process simply diminishes the catalytic activity of the dust. In order to test this hypothesis, some carefully purified benzene dried by calcium chloride was freed from dust by distillation without ebullition[6] and the boiling point determined.[53] The temperature of the benzene was raised very slowly to 100°, but at this point boiling commenced and the temperature fell to 80°, the normal boiling point. This experiment is not, however, decisive because the benzene was found to contain a large quantity of motes apparently detached from the glass by the violent ebullition. Further work along these lines indicated that the dust alone is not the deciding factor in the boiling and evaporation of liquids; measurements showed that the rate of evaporation or condensation in the dust-free condition is the same as when dust is present. It may be, however, that the change of state from a liquid to a gas is a catalytic phenomenon which requires a *moist* surface; if this is so, Baker's results become explicable because not only must the liquid and the surface of the vessel be dry but the dust particles also; undoubtedly the last process would be very slow.

Summary

All chemical reactions proceeding under the usual conditions do so in the presence of great numbers of suspended dust particles; these are the cause of a number of anomalous results in certain supposedly homogeneous reactions.

The thermal decomposition of hydrogen peroxide occurs mainly on dust particles but partly on the surface of the vessel; there is no evidence of any homogeneous decomposition. The thermal oxidation of sodium sulfite

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[51] Chapin, *J. Ind. Eng. Chem.*, **6**, 1002 (1914). See also Reinders and Vles, *Rec. trav. chim.*, **44**, 29 (1925).

[52] Baker, *J. Chem. Soc.*, **121**, 568 (1922).

[53] This experiment was performed at New York University with Mr. W. A. Wesolowski in January, 1924. Recently a very comprehensive study of this phenomenon has been published in which a similar experiment with ether yielded negative results. See Kenrick, Gilbert and Wismer, *J. Phys. Chem.*, **28**, 1297 (1924).

is almost entirely a dust reaction, for when the dust is removed the rate of oxidation is immeasurably slow.

The photochemical decomposition of hydrogen peroxide occurs largely on the surface of suspended dust; when this is removed, the quantum yield is very greatly diminished. It seems likely that when reactions of large quantum yield are studied in the dust-free condition the Einstein photochemical equivalence law will hold. We may explain this by assuming that the substrate is adsorbed in isolated aggregates, the average size of which is given by some multiple of the quantum yield of the reaction; a single quantum of light absorbed by one molecule of the aggregate is supposed to "explode" the whole aggregate.

There are two classes of reactions in which the phenomenon of negative catalysis appears. The first class is homogeneous and consists mainly of those reactions which occur in anhydrous organic solvents or 100% sulfuric acid and are inhibited by small amounts of water. The second class is heterogeneous and inhibitors or accelerators simply poison or promote the catalytic activity of dust particles or the walls of the containing vessel.

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PARAMETERS IN CRYSTAL STRUCTURE. THE MERCUROUS HALIDES

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In the analysis of crystal structure by means of X-rays it is necessary to make a calculation of the intensities of X-ray reflection from different crystal planes for various atomic arrangements and to compare the calculated intensities with those observed. Unless the atomic positions are completely determined by the symmetry of the crystal, there will be one or more undetermined parameters which can be evaluated only with the aid of the intensity data; the values obtained for the parameters will be correct if the method of calculating the intensity of reflection is correct. Unfortunately, the expression that is used in the calculation of the intensity of reflection contains an empirical factor called the "structure factor," depending upon the atomic and electronic arrangement in the crystal, which is but vaguely understood. The two points about which most uncertainty exists are: (1) the relation between the intensity of reflection and the structure factor and (2) the correct method of calculating the structure factor from any given atomic arrangement.

The purposes of this paper are: (1) to discuss the bearing of recent

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[1] National Research Fellow.

experiments by the author on these two points and (2) to describe a method of determining the parameters in a crystal which does not require a previous knowledge of the structure factor, and to apply this method to the determination of the parameters in the crystal structure of the mercurous halides.

The Structure Factor.—Darwin's expression[2] for the intensity of reflection of X-rays at an angle Θ from the face of a single crystal may be written

$$I \propto f^2 e^{-\frac{b^2 \sin^2\Theta}{\lambda^2}} \frac{1 + \cos^2 2\Theta}{\sin 2\Theta} = F^2 \frac{1 + \cos^2 2\Theta}{\sin 2\Theta} \qquad (1)$$

leaving out of consideration all the factors in the original equation which are independent of the angle of reflection for a certain crystal. The factor f is a function of $\lambda/\sin\Theta$ and of the electronic (and atomic) arrangement in the unit cell; $e^{-(b^2 \sin^2\Theta)/\lambda^2}$, the Debye temperature factor, is a similar function. Owing to the difficulty of evaluating the Debye factor, it may be included with f in a new factor F, called the "structure factor." This F represents the amplitude of the diffracted wave, and is equal to the number of electrons in the unit cell at zero angle of reflection, when $\sin\Theta = 0$; as the angle of reflection increases, F falls off in a manner dependent upon the electronic distribution in the unit cell. Each atom contributes to F and, since atoms of different kinds with different electronic arrangements may exist in the unit cell, the resultant value of F depends in a complicated way upon Θ.

In all efforts to get a working formula for the intensity of reflection, simplifying assumptions have been made. For example, Wyckoff[3] gives an expression which is generally used in this country

$$I \propto \left(\frac{d_{(hkl)}}{n}\right)^{2.35} (A^2 + B^2) \qquad (2)$$

where $A = \sum\limits_s \overline{N}_s \cos 2\pi n(hx_s + ky_s + lz_s)$ and $B = \sum\limits_s \overline{N}_s \sin 2\pi n(hx_s + ky_s + lz_s)$. $\overline{N}_s$ is the number of electrons in the sth atom located at x_s, y_s, z_s, and the summation is taken over each atom in the unit cell; $(A^2 + B^2)$ is the resultant intensity due to the superposition of diffracted waves from each atom in the unit cell, assuming the atom to have its diffracting power proportional to its electron content and concentrated at the atomic center—this factor is included in the F^2 of Equation 1; $\left(\frac{d_{(hkl)}}{n}\right)^{2.35}$ includes the part of Equation 1 which depends upon the angle of reflection, that is, the decrease of F with increasing Θ as well as the factor $(1 + \cos^2 2\Theta)/\sin 2\Theta$. *In the use of Expression 2 the tacit assumption is made that F varies with Θ in the same way for every atom in the unit cell,* an assumption evidently not based on fact.

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[2] Darwin, *Phil. Mag.*, **43,** 800 (1922).

[3] Wyckoff, "Structure of Crystals," Chemical Catalog Co., **1924,** p. 107.

However, very satisfactory results have been obtained by the use of expressions like Expression 2 for the determination of parameters in crystal structure. The reasons for the trustworthiness of determinations based upon this expression are: (1) a small change in the value of a parameter makes a large change in the structure factor for certain reflections; (2) if diffraction data are used to the fullest extent, so many comparisons of intensity are possible that a balancing of errors takes place; (3) the variation of F with Θ does not differ a great deal for heavy atoms at small angles of reflection, so that the assumption underlying Expression 2 perhaps becomes justified. Expression 2 fails completely for light atoms, consequently the parameters describing the positions of light atoms in crystals are rarely determined with accuracy.

Intensity of Reflection and the Structure Factor.—That the intensity of reflection is proportional to the square of the structure factor is indicated by Equation 1; but experimental data for certain very perfect crystals (diamond, calcite, aragonite) show that the measured intensity in these few instances is more nearly proportional to the first power of the structure factor. The theoretical treatment of X-ray reflection by Ewald[4] leads to the conclusion that the intensity should be proportional to the first power of the structure factor in the case of a *perfect* crystal. Darwin's treatment of reflection by a perfect crystal leads to the same result when we consider the abnormal absorption at the reflecting angle which he calls "extinction." In a perfect crystal with a thickness greater than 10^{-5} cm., the intensity of reflection will be modified by extinction. Darwin distinguishes two kinds of extinction: *primary* extinction, which occurs within each little block that acts as a perfect crystal, and *secondary* extinction, which represents the shielding of the blocks deep within the crystal by the reflection of the X-rays from the blocks near the surface. Extinction increases the effective absorption coefficient at the reflecting angle and, in case the crystal is nearly perfect, may cause an increase that quite swamps the effect of normal absorption. James and Wood[5] and W. L. Bragg[6] have shown that, since extinction is proportional to the intensity of reflection, the measured intensity would be proportional to the first power of the structure factor in the case of a perfect crystal.

Now it is doubtful whether many substances form even approximately perfect crystals. Microscopically, most crystals are probably mosaic structures, with the size of the perfect crystal blocks of the order of 10^{-4} cm. or even less. Secondary extinction, though, exists in an imperfect crystal and may cause a reduction of perhaps 40% in the intensity of the strongest reflections from a crystal. Consequently, intensity data from

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[4] Ewald, *Physik. Z.*, **26**, 29 (1925).

[5] James and Wood, *Proc. Roy. Soc.*, (London), **109A**, 598 (1925).

[6] W. L. Bragg, *Phil. Mag.*, **50**, 306 (1925).

single crystal measurements may well be greatly in error. Secondary extinction becomes negligible when the thickness of the crystal becomes less than 10^{-2} cm.; therefore powder measurements are free from its effect. Recent experiments by the author[7] on the intensity of reflection of crystal powders of various particle sizes have shown that primary extinction is absent from crystal powders that have been thoroughly ground. We may conclude, therefore, that the intensity of reflection from powdered crystals is proportional to the square of the structure factor.

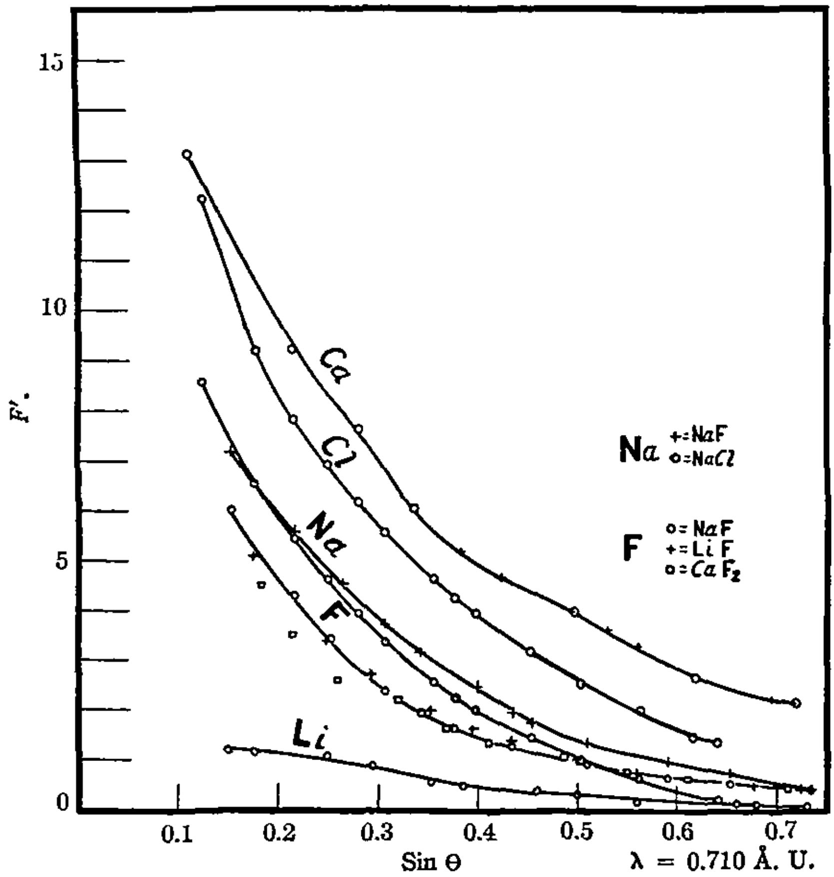

Fig. 1.—Atomic-structure factor curves.

Calculation of the Structure Factor.—We have seen that the ordinary method of calculating the structure factor in the expression by which we test the fitness of any proposed crystal structure assumes that the variation of F with Θ is the same for every atom in the unit cell. This assumption is in error, especially for light atoms, when the unit cell contains more than one kind of atom. The author has measured the relative intensities of reflection from different planes of pure sodium fluoride, lithium fluoride, calcium fluoride and sodium chloride, and obtained the F curves for the dif-

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[7] Havighurst, *Proc. Nat. Acad. Sci.*, **12**, 375, 380 (1926).

ferent atoms.[7] These curves are shown in Fig. 1, where the atomic structure factor is plotted against sin Θ. The structure factor is called F' because while the Na and Cl curves from sodium chloride are correct in absolute magnitude, the other curves have been evaluated indirectly and may be in error on the absolute scale by perhaps 10%. Curves from two different substances should not, strictly speaking, be compared unless their absolute magnitudes have been determined accurately; but curves for different atoms in the same crystal (sodium and fluorine, calcium and fluorine, lithium and fluorine, sodium and chlorine) are comparable. The ratios of the ordinates of the curves for different values of sin Θ have been tabulated in Table I. The ratios from any pair of curves should be constant if the variation of F with sin Θ is the same for the two atoms. Inspection of the table shows that these ratios vary widely.

TABLE I

RATIOS OF *F* CURVES

$\lambda = 0.710$ Å.

Sin Θ	0 (assumed)	0.15	0.20	0.20	0.40	0.50	0.60	0.70
Ca^{++}/F^{-}	1.8	1.90	2.10	2.84	3.41	3.95	4.54	4.85
Na^{+}/F^{-}	1.0	1.20	1.28	1.56	1.69	1.40	1.46	1.22
Na^{+}/Cl^{-}	0.55	0.70	0.72	0.62	0.51	0.40	0.25	(0.15)
Li^{+}/F^{-}	.20	.20	.24	.33	.34	.30	.31	.22
Cl^{-}/F^{-}	1.8	1.76	1.79	2.30	2.72	2.60	2.46	2.23
$Ca^{++}/Na^{+}_{(NaF)}$	1.8	1.58	1.65	1.82	2.02	2.82	3.00	3.96
$Na^{+}_{(NaF)}/Li^{+}$	5.0	6.12	5.30	4.70	5.00	4.67	4.75	5.50

Two conclusions may be drawn from these results: (1) a positive ion has a larger F value than a negative ion with the same number of electrons, because the excess positive charge draws the electronic atmosphere in toward the nucleus, and electrons close to the nucleus reflect more strongly in the angular domain covered by ordinary crystal structure work; (2) a heavy ion has larger relative F values than a light ion of the same sign; this, too, because the heavier ion has its electrons nearer the nucleus. It is evident that the use of Expression 2 in calculating the structure factor is especially undesirable in the case of crystals containing ions of opposite sign, or in the case of crystals containing both heavy and light atoms.

The use of experimental F curves of the type shown would allow much more accuracy in the calculation of the structure factor. Here too, however, there is an objection, because the F curve depends not only on the specific atom or ion, but also upon the crystal lattice forces to which the atom is subjected; for example, the curve for sodium in sodium fluoride differs from that for sodium in sodium chloride. On the other hand, the curves for fluorine from lithium fluoride, sodium fluoride and calcium fluoride are all quite similar. The crystal lattice forces in the two sodium salts must be of an appreciably different magnitude, while in the fluorides they are nearly equal.

Another method of determining F curves is that of Hartree,[8] which is based upon the dimensions of the electronic orbits as determined from spectral data, and the distribution of the electrons in these orbits as given in Stoner's scheme. James and Wood[5] have used these curves with satisfactory results. Hartree's method does not take into consideration the effect of thermal vibration, which greatly reduces the actual F curves at large angles; for this and perhaps other reasons, his curves are not in good agreement with experimental curves in the few cases where comparison is possible.

There is no existing method of predicting the structure factor with quantitative accuracy, although crystal structure work based on the use of F curves gotten experimentally or by Hartree's method would be superior to that based only on the use of Expression 2. Yet at least a qualitative knowledge of the structure factor has been essential to every determination of a parameter in a crystal. *There is another method of determining the parameters in a crystal* which depends only upon experimental data and upon assumptions that are more easily defended than those upon which the theory of the structure factor is based. This method consists in the determination of the positions of greatest density of diffracting power in the unit cell of a crystal by the use of a Fourier's series.

The Use of Fourier's Series in Determining Parameters.—Duane[9] has shown that the distribution of density of diffracting power (we shall call it "electron density") in a crystal may be represented by a Fourier series whose general term is

$$A_{n_1n_2n_3} \sin\left(2\pi \frac{n_1X}{a_1} - \delta_{n_1}\right) \sin\left(2\pi \frac{n_2Y}{a_2} - \delta_{n_2}\right) \sin\left(2\pi \frac{n_3Z}{a_3} - \delta_{n_3}\right) \quad (3)$$

where $n_1n_2n_3$ are the Miller indices (multiplied by the order of reflection) of any reflecting plane; a_1, a_2, a_3 are the lengths of the sides of the unit cell; the δ's are phase constants; $An_1n_2n_3$ is the F of Equation 1. Duane's work was based upon a quantum theory of diffraction, but A. H. Compton[10] has recently obtained a similar expression for the electron density on the basis of the classical theory of diffraction. In order to determine the positions of the atoms with the aid of this series, we must make two assumptions: (1) the distribution of diffracting power conforms to the symmetry of the crystal; (2) a point of maximum density is the center of an atom. As a result of the first assumption we are often enabled to fix the phase constants in Expression 3. Then, if the series is evaluated with the aid of experimental data on the intensity of reflection from the different crystal planes, there will be maxima in the curve representing electron density which we assume to be the centers of atoms;

[8] Hartree, *Phil. Mag.*, 50, 289 (1925). W. L. Bragg, *ibid.*, 50, 306 (1925).

[9] Duane, *Proc. Nat. Acad. Sci.*, 11, 489 (1925).

[10] Compton, *Phys. Rev.*, 27, 510 (1926).

there is no *a priori* assumption of the existence of atoms or molecules in the crystal. Electron-density curves have been obtained by the author[11] for some simple crystals. In many cases the difficulty of this procedure is very great because the symmetry of the crystal is so low that the series expressing electron density is a complicated one containing both sines and cosines; but sometimes the crystal possesses so much symmetry that the parameters may readily be obtained from a simple series. For example, if the plane of the X and Y axes of a crystal is a plane of symmetry and the intersection of the two axes is taken as the origin, the series representing the electron density in a direction Z, perpendicular to the plane of symmetry, will contain cosines only, for the electron density must be symmetrical with respect to the plane of symmetry. The δ_n of Expression 3 is, therefore, an odd multiple of $\pi/2$. Such a series may easily be evaluated. As an example of the method, the parameters the mercurous halides will be determined.

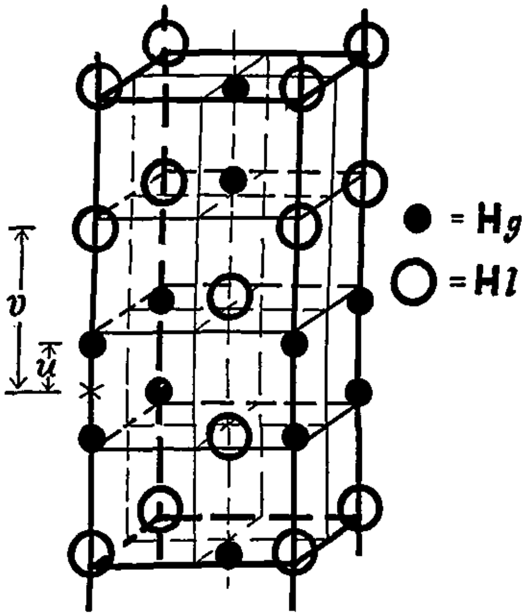

Fig. 2.—Atomic arrangement of mercurous halides.

Parameters of the Mercurous Halides.—The crystal structure of these substances has been investigated by the author,[12] who used the powdered-crystal method of X-ray analysis supplemented by reflections of the tungsten K series from single crystal faces of calomel. The crystals are tetragonal, with two molecules of mercurous halide (Hg_2Hl_2) in the unit cell. The atomic arrangement can be obtained from any of the space groups D_{4h}^{17}, D_{4h}^{15}, D_{4h}^{14}, D_{4h}^{12}, D_{4h}^{6}, D_{4h}^{4}, D_{4}^{9}, D_{4}^{6}. There are four mercury atoms at $00u$; $00\bar{u}$; $^1/_2, {}^1/_2, {}^1/_2 + u$; $^1/_2, {}^1/_2, {}^1/_2 - u$; and four halogen atoms at $00v$; $00\bar{v}$; $^1/_2, {}^1/_2, {}^1/_2 + v$; $^1/_2, {}^1/_2, {}^1/_2 - v$. The dimensions of the unit cells and the values of the parameters as previously determined are given in Table II. Fig. 2 shows the unit cell. The molecule Hl-Hg-Hg-Hl seems to exist in the crystal, the orientation of this molecule being the reason for the unique character of the Z axis. Expression 2 was used in the determination of the parameters, and further simplifying assumptions were made as follows: (1) the absolute distance Hg-Hg

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[11] Havighurst, *Proc. Nat. Acad. Sci.*, **11**, 502, 507 (1925).

[12] Havighurst, *Am. J. Sci.*, **10**, 15 (1925).

is the same in each substance; (2) $v - u = 0.25$ in each crystal. Although it was recognized that these assumptions might lead to inaccuracy in the values of the parameters, they were introduced for the sake of simplicity in the calculations.

TABLE II

CRYSTAL STRUCTURE OF THE MERCUROUS HALIDES

Crystal	c, Å.	a, Å.	u	v
Hg_2Cl_2	10.89	4.47	0.110	0.360
Hg_2Br_2	11.10	4.65	.108	.358
Hg_2I_2	11.61	4.92	.105	.355

Recently Hylleraas[13] has published some work on the crystal structure of the mercurous halides. His structure is identical with that of the author, but he does not claim to have located the parameters accurately.

It is evident that the origin of the unit cell is a center of symmetry. Consequently the Fourier's series expressing the electron density at a point in the unit cell will be a simple cosine series,

$$\rho_{(XYZ)} = \sum_{n_1}\sum_{n_2}\sum_{n_3} A_{n_1n_2n_3} \cos 2\pi \frac{n_1X}{a} \cos 2\pi \frac{n_2Y}{a} \cos 2\pi \frac{n_3Z}{c} \qquad (4)$$

for the phase constants are all odd multiples of $\pi/2$; but the origin is midway between two atoms, and therefore is a point of minimum (probably zero) electron density. Some of the coefficients must accordingly be negative, so that the sum of the series shall be approximately zero at the origin. A qualitative knowledge of the values of the parameters, such as can be obtained by inspection of the relative intensities, is sufficient to determine the signs of the coefficients.

We are interested in evaluating the series representing the electron density along the Z axis. This series is

$$\rho_{(OOZ)} = \sum_{n_1}\sum_{n_2}\sum_{n_3} A_{n_1n_2n_3} \cos 2\pi \frac{n_3Z}{c} \qquad (5)$$

A preliminary study of the relative intensities shows that the values of u and v must be slightly less than $^1/_8$ and $^3/_8$, respectively. Now it seems probable that when Z/c is slightly less than $^1/_8$, at the center of the mercury atom, the series will have its maximum value and the coefficients will all be positive. The assumption that the coefficients of the first few terms of the series (which are all that we can measure experimentally) are positive at the center of a mercury atom, that is, when Z/c is slightly less than $^1/_8$, fixes the signs at the origin. This method of determining the signs of the terms in the series may be considered too intuitive, but it is substantiated by a rigorous method which we shall carry through.

The unit cell of Hg_2Hl_2 is composed of four interpenetrating body-centered lattices, two of mercury and two of halogen, with origins at $00u$, $00\bar{u}$, $00v$, $00\bar{v}$, respectively. The electron density, due to its

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[13] Hylleraas, *Physik. Z.*, **26**, 811 (1925).

own electrons, at a point in any of these lattices (the origin of each is a center of symmetry for that lattice) may be represented by a Fourier's series as in Equation 4. We wish to superimpose these four series, so as to get an expression for the total electron density due to all four lattices.

The coefficients in the four series are $A'_{n_1n_2n_3}$, $A''_{n_1n_2n_3}$, $B'_{n_1n_2n_3}$, $B''_{n_1n_2n_3}$, where $A' = A'' \propto F_{\mathrm{Hg}}$ and $B' = B'' \propto F_{\mathrm{HI}}$. Now change the origin of each of the four lattices to the point (000). The total electron density is the sum of the contributions from the four separate lattices:

$$\begin{aligned}\rho(xyz) = {} & \sum_{n_1}\sum_{n_2}\sum_{n_3} A'_{n_1n_2n_3} \cos 2\pi \frac{n_1X}{a} \cos 2\pi \frac{n_2Y}{a} \cos\left(2\pi \frac{n_3Z}{c} + 2\pi n_3u\right) + \sum_{n_1}\sum_{n_2}\sum_{n_3} A''_{n_1n_2n_3} \\ & \cos 2\pi \frac{n_1X}{a} \cos 2\pi \frac{n_2Y}{a} \cos\left(2\pi \frac{n_3Z}{c} - 2\pi n_3u\right) + \sum_{n_1}\sum_{n_2}\sum_{n_3} B'_{n_1n_2n_3} \cos 2\pi \frac{n_1X}{a} \cos 2\pi \frac{n_2Y}{a} \\ & \cos\left(2\pi \frac{n_3Z}{c} + 2\pi n_3v\right) + \sum_{n_1}\sum_{n_2}\sum_{n_3} B''_{n_1n_2n_3} \cos 2\pi \frac{n_1X}{a} \cos 2\pi \frac{n_2Y}{a} \cos\left(2\pi \frac{n_3Z}{c} - 2\pi n_3v\right) \\ = {} & \sum_{n_1}\sum_{n_2}\sum_{n_3} (A' + A'')_{n_1n_2n_3} \cos 2\pi \frac{n_1X}{a} \cos 2\pi \frac{n_2Y}{a} \cos 2\pi \frac{n_3Z}{c} \cos 2\pi\, n_3u + \sum_{n_1}\sum_{n_2}\sum_{n_3} \\ & (B' + B'')_{n_1n_2n_3} \cos 2\pi \frac{n_1X}{a} \cos 2\pi \frac{n_2Y}{a} \cos 2\pi \frac{n_3Z}{c} \cos 2\pi n_3v \\ = {} & \sum_{n_1}\sum_{n_2}\sum_{n_3} \left[(A' + A'') \cos 2\pi n_3u + (B' + B'') \cos 2\pi n_3v\right]_{n_1n_2n_3} \cos 2\pi \frac{n_1X}{a} \cos 2\pi \frac{n_2Y}{a} \\ & \cos 2\pi \frac{n_3Z}{c} \qquad (6)\end{aligned}$$

The F^2 of Equation 1, which is what we actually measure, is proportional to the square of the quantity in the brackets, while the sign of the quantity in the brackets is determined by the signs of $\cos 2\pi n_3u$ and $\cos 2\pi n_3v$. In case the signs of these two factors are different, it will be remembered that $(A' + A'') > (B' + B'')$. From Equation 6 we find that the first few coefficients are all positive at the center of a mercury atom (when $u = Z/c$), which is the conclusion at which we had previously arrived.

We are now in a position to evaluate Series 5. As coefficients in the series we shall use the F values obtained from the estimated intensities of the powder reflections as follows[7]

$$F^2 \propto \frac{I}{j} \frac{\sin^2\theta \cos\theta}{1 + \cos^2 2\theta} \qquad (7)$$

where j is the number of planes belonging to the form which is reflecting the X-rays. Intensity estimates from powder-method photographs are not at all accurate, but a purpose of this work is to show that the parameters may be determined from the same data as those used previously. As a matter of fact, the inaccuracy of the estimated intensities is of surprisingly small moment; this will be shown later.

The intensity data, given in Table III, are those used in the previous determination of the parameters. The only difference is that the intensity of the hazy reflections from the (200) and (204) planes, which was underestimated because of the diffuseness of the lines of the films, has been

Table III

Intensities of X-Ray Reflection for the Mercurous Halides

		Hg_2Cl_2				Hg_2Br_2			Hg_2I_2		
		Ionization method		Photographic method							
	Plane	*I*	*F*	*I*	*F*	Plane	*I*	*F*	Plane	*I*	*F*
8	101	100	5.40	90	5.13	101	40	3.32	101	15	1.87
4	110	100	10	100	10	110	100	10	110	100	10
8	103	25	2 39	10	2.52	004	40	10 7	004	30	9.21
2	004		6.61	30	9.06	200	40	9 21	200	40	9 01
4	200	39	8.94	40	9.05	114	60	8 46	114	55	8 39
8	114	44	7.28	50	7.77	121	15	3.17	121	6	1.97
16	121	58	4.26	70	4.64	105	35	7.00	105	30	6.43
8	105		6.46		7.05	204	35	7.81	204	35	7.90
16	123	34	1.60	35	1.60	220	15	8.01	220	20	9 05
8	204		7.37		7.49	125	25	5.63	125	20	4 97
4	220	11.5	7.02	15	8.01	130	10	5.19	130	15	6 28
2	004		6.61	30	9.06	224	20	7.67	224	20	7.52
8	301	27	3.51	25	3.33	008	4	7 00	008	4	6.97
16	125		5.20		4.96	134	20	6.00	134	20	5 86
8	130	9.5	5.07	8	4.64	231	15	2.35			
8	224	10	4.86	15	5.96	118		5.10	118	10	4.03
2	008		4.86		5.44	305		4.71	305		4 46
16	134	22	4.41	20	5.14	109	20	6.90	109	20	7.38
8	118		4.20		4.08	208		6.23	208		5.41
16	231		2.33	8	2.69	235	5	3.53	235	7	4.11
8	305		3.30		3 81				330	4	6.27
8	109	12	5.38	15	5.76	404	15	5.82	404	4	4.64
8	208		4.55		4.99	129		4.45	228	15	4.03
16	141	5	2.23	6	2.23	228		3.36	129		5.70
16	235		3.16		3.16	334	4	3.06	334	4	4 85
16	129	14	4.37	15	4.52	138		2.17	138	4	2.49
8	404		4.67		4.96	145		2.17	145		2.49
8	228		4 05		4 05	244	4	3 21	244	6	3 86
8	334	5	3.04	4	2.49	309		2 63	309		3.16
16	138		2.49		2.15						
16	145		2.49		2.15						
8	309	3.5	2.62	6	3.20						
16	244		2.93		3.93						

increased. The relative intensities of the reflections from powdered mercurous chloride were remeasured by an ionization method previously described,[7] and are also shown in Table III. They show that the powder-method estimates, although only approximate, contain no systematic error.

One difficulty inherent in the application of the powdered-crystal method to any crystal analysis is that reflections are often superimposed, and the total intensity must be divided arbitrarily among the components. By analogy with single reflections from the same classes of planes, this division may be made with some accuracy, or the structure factor approximated by Expression 2 may be used. In either case a certain amount of uncertainty is introduced.

The powder-method estimates of intensity in Table III have been used to evaluate Series 5 for each of the mercurous halides, and the curves of electron density, $\rho_{(00z)}$, are shown in Fig. 3. The parameters may be read directly from the curves. It is remarkable that these parameters should be so nearly equal for the three substances; this equality means that, as bromine is substituted for chlorine and iodine for bromine, the distance between mercury atoms increases in proportion to the increase in size of the unit cell. The best values for the parameters are u = 0.116, v =

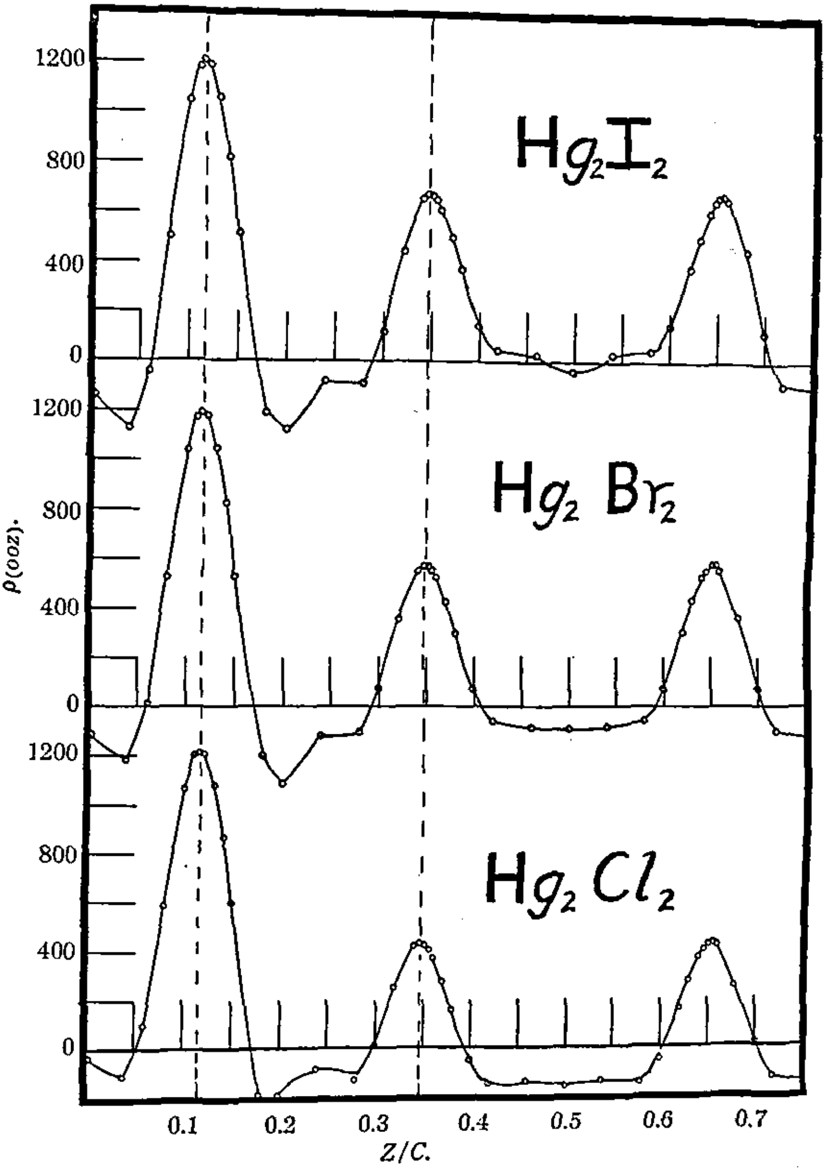

Fig. 3.—Electron-density curves.

0.347.[14] The ionization measurements on mercurous chloride when used in the series give a curve agreeing so nearly with that of Fig. 3 that it can not well be drawn in as a separate curve. Upon consideration it will be seen that fortuitous errors in the intensity estimates will not cause much error in the electron density curves at their maxima, because the density is the sum of contributions from a number of different terms, the errors of which have a tendency to neutralize each other.

The chief advantage of this method of determining the parameters in a crystal is that it automatically sums up all of the available data and gives a result which depends upon no assumed knowledge of the structure factors of the atoms in the crystal. It must be remembered that we have used relative intensities only in evaluating the series, so our electron-density values are only relative. To get the absolute electron density, it would be necessary to have the absolute values of F for all the planes of the crystals. Reflections of such small intensity that they are not observed on the powder-method photographs would have to be measured. Such a procedure would change the scale of ordinates in Fig. 3 to an absolute scale of electron density, and smooth off the minima, bringing them up to the zero line at the same time. Curves of this type have been obtained by the author for the alkali halides, but such refinements would have little effect upon the positions of the maxima on the curves, which are what we are primarily interested in here.

The author is indebted to Professor William Duane for his suggestions and advice in connection with this work.

Summary

In the determination of parameters in crystal analysis, the intensity of reflection of X-rays must be used to evaluate the structure factor. Experiments show that intensities of reflection measured by the powdered-crystal method are accurately proportional to the square of the structure factor. The usual method of calculating the structure factor for a crystal is based upon the assumption that the atomic structure factors of the component atoms vary in the same manner with the angle of reflection. This assumption is not valid, and is particularly in error for crystals containing light elements and ions of opposite charges, as is shown by F curves obtained experimentally for the atoms in lithium fluoride, sodium fluoride, calcium fluoride and sodium chloride.

For accurate determination of parameters in crystal structure, either F curves for the individual atoms should be used, or some method requiring no knowledge of the F curves. Such a method consists in the use of a

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[14] Huggins and Megill, working at the California Institute of Technology, have recently worked out the structure of mercurous iodide, using Laue photographs and rotation spectra. Their values for the parameters are $u = 0.117$, $v = 0.353$.

Fourier's series to determine the electron density at points in the unit cell of a crystal, the coefficients of the series being evaluated from the measured intensities of X-ray reflection. This method, when applied to mercurous chloride, mercurous bromide and mercurous iodide, sets the values of the parameters at $u = 0.116$, $v = 0.347$ in the unit cell containing two molecules of mercurous halide with mercury atoms at $00u$; $00\bar{u}$; $^1/_2, ^1/_2, ^1/_2 + \bar{u}$; $^1/_2, ^1/_2, ^1/_2 - u$; and halogen atoms at $00v$; $00\bar{v}$; $^1/_2, ^1/_2, ^2/_2 + v$; $^1/_2, ^1/_2, ^1/_2 - v$.

CAMBRIDGE, MASSACHUSETTS

NOTES

Reaction of "Aluminon" with Hydroxides of Beryllium, Rare Earths, Zirconium and Thorium.—The new reagent for aluminum, proposed by Hammett and Sottery[1] and now on the market under the trade name "Aluminon," has proved very satisfactory in our Laboratory. Its value for the detection of very small amounts of aluminum has been shown recently by Lundell and Knowles.[2]

It appears worth recording that lakes are formed by this reagent with the hydroxides or basic acetates of beryllium, yttrium, lanthanum, cerium, neodymium, erbium, zirconium and thorium. All these are deeper red than the aluminum lake, the color being a rich bright crimson, that with cerous hydroxide much darker than the others. All, except that of beryllium, are either dissolved or decolorized by moderate additions of ammonium carbonate. Accordingly, the reagent does not distinguish aluminum from beryllium in mixtures of the two hydroxides. The lakes are not affected by moderate concentrations of ammonia except that of zirconium which is partially decolorized and flocculates as a rose-pink precipitate. All are distinctly more insoluble than the corresponding hydroxides or basic acetates.

From the commercial pure nitrates, solutions were made up containing approximately 10, 1 and 0.1 mg. of the element per cc., except the beryllium solutions which contained 2, 0.2 and 0.02 mg. of the element per cc. To 1 cc. of these solutions was added 5 cc. of 1 N hydrochloric acid, 5 cc. of 3 N ammonium acetate, 5 cc. of 0.1% Aluminon solution and, after mixing, 3 cc. of 6 N aqueous ammonia. Further addition of 2 cc. of 9 N aqueous ammonium carbonate sufficed to dissolve or decolorize the precipitates except in the case of beryllium. Distinct precipitates were formed by 1 mg. of each of the elements tested (0.2 mg. of beryllium). Pink solutions, but no precipitates formed when 0.1 mg. (0.02 mg. of beryllium) was taken. The pink color of these very dilute solutions was not

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[1] Hammett and Sottery, THIS JOURNAL, 47, 142 (1925).

[2] Lundell and Knowles, *Ind. Eng. Chem.*, 18, 60 (1926).

altered by aqueous ammonia even after several days, except in the case of zirconium where aqueous ammonia rapidly discharged the color.

The following experiments show the smaller solubilities of the lakes compared with the solubilities of the corresponding hydroxides or basic acetates. Mixtures of 1 cc. of solution (10 mg. of the element), 5 cc. of 1 *N* hydrochloric acid and 5 cc. of 3 *N* ammonium acetate became distinctly turbid as soon as 5 cc. of Aluminon solution was added, except in the cases of aluminum and erbium which remained clear for several hours, but on standing overnight deposited precipitates. Precipitation in all these cases was incomplete and the supernatant liquids remained red or pink. The fraction precipitated seemed to vary between roughly one-fifth and one-third. The zirconium lake precipitated under these conditions was brilliant scarlet-red in contrast to the rose-pink color of that formed in the presence of ammonia. Likewise the aluminum lake similarly precipitated is deep crimson, much darker than that formed in the presence of ammonia. It appears that ammonia exerts an appreciable bleaching action on both of these lakes. Mixtures in which the Aluminon solution was replaced by an equal volume of water all remained perfectly clear after 24 hours.

The beryllium lake is much less soluble in ammonium carbonate than is beryllium hydroxide. A precipitate of the latter containing 2 mg. of the element dissolved completely when the liquid was made 3 *N* in ammonium carbonate while the lake containing the same amount of element was only partially dissolved when the liquid was made 5.5 *N* in carbonate.

A peculiar action was observed in the case of the lanthanum solution and in this alone. In the presence of ammonia the crimson lake settled rapidly, leaving the supernatant liquid colorless. Thereafter a considerable amount of pure white precipitate gradually flocculated which settled slowly and tended to cling to the walls of the vessel. After 24 hours a sharp line of demarcation between the heavier red and lighter white precipitates was visible. The cause of this phenomenon is not immediately apparent since impurities likely to be found in a lanthanum preparation should adsorb the dye equally well.

Thallic hydroxide is not precipitated in the presence of ammonium acetate but when the usual addition of Aluminon was made before adding ammonia the solution remained red for some days and a small amount of reddish precipitate was gradually deposited.

A scandium salt was not available. It would be of interest to know the behavior of Aluminon toward scandium hydroxide.

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A. R. MIDDLETON

RECEIVED JULY 2, 1925
PUBLISHED AUGUST 5, 1926

The Isomeric Chlororutheniates.—In a recent number of THIS JOURNAL Howe and Haynes[1] have referred to my paper on the potassium chlororutheniates[2] and it is necessary for me to correct certain inaccuracies in their communication.

According to Howe and Haynes "Briggs considers that the normal alpha salt is a monohydrate, $K_2RuCl_5.H_2O$, in which ruthenium has a coördination number of 6," also "Briggs gives to the aquo salt the formula $2K_2RuCl_5.3H_2O$......It is difficult to see how so slight a difference in hydration could occasion so profound a difference in properties."

As a matter of fact the third paragraph of my paper reads as follows: "It has been found that in Miolati's series (alpha series) there are at least two compounds having the formulae $K_2RuCl_5.H_2O$ and $2K_2RuCl_5.3H_2O$, respectively. In Howe's series (aquo series) the only salt prepared in the pure state had the formula $2K_2RuCl_5.3H_2O$, although some slight evidence was obtained for the existence of other compounds having the formulae $K_2RuCl_5.H_2O$ and $K_2RuCl_5.2H_2O$." In the seventh paragraph of my paper I expressed the view that ruthenium probably functions with the coördination number 8 in all these compounds. Reference was also made to the possibility that the coördination number may be different in the two series, namely, seven in the one and eight in the other, but *nowhere* have I suggested a coördination number six as stated by Howe and Haynes.

Again, in referring to the compound $K_2RuCl_5.K_2RuCl_5OH$ which I obtained from the aquo salt by bubbling air through the heated, strongly acid solution, Howe and Haynes suggest "This would seem to be the ordinary alpha salt, partially in the anhydrous form and partly the monohydrate." The oxidation product, however, is quite different in properties (crystalline form, solubility and color) from the alpha salt.

The existence[2] of such substances as $2K_2RuCl_5.3H_2O$ (with constitutional water), $K_2RuCl_5.K_2RuCl_5OH$ and $K_5Ru_3Cl_{14}.3H_2O$ shows that in the chlororutheniates there is a polynuclear complex in which chloride ions or water molecules are shared by the ruthenium ions. Various cases of isomerism are then possible according to the particular components which are shared.

Assuming a binuclear complex and coördination number of eight, then if the coördinated ions or molecules are arranged around the ruthenium ion, not at the corners of a cube but at the corners of the polyhedron obtained by rotating one face of a cube in its own plane[3] through 45°, either two, three or four components may be shared, the two polyhedra in the complex having a common edge, a common triangular face or a common square face respectively. With a common edge the formula would be $2K_2RuCl_5.4H_2O$.

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[1] Howe and Haynes, THIS JOURNAL, 47, 2920 (1925).

[2] Briggs, *J. Chem. Soc.*, 127, 1042 (1925).

[3] This figure gives the stable arrangement of eight electrons around a positive core according to Foppl [see J. J. Thomson, *Phil. Mag.*, 41, 515 (1921)].

A common triangular face would give $2K_2RuCl_5.3H_2O$, and a common square face $2K_2RuCl_5.2H_2O$. Owing to the comparatively slight solubility of the alpha salts, and the ease with which both series undergo hydrolysis in neutral solution, molecular-weight determinations would have little value, and I therefore suggested in my paper the desirability of an X-ray investigation of these substances which I personally, however, am not in a position to undertake.

Charonnat's Views.—The suggestion made by Charonnat[4] that the alpha series contain quadrivalent ruthenium appears improbable for the following reasons in addition to those mentioned by Howe and Haynes: (1) the alpha series is formed directly from $RuCl_3$ and KCl as observed by Miolati and Tagiuri[5] and by Gutbier, Falco and Vogt;[6] (2) a reducing agent is not necessary to convert the alpha salt into the aquo salt; this change can be brought about by hydrochloric acid alone;[2] (3) by oxidizing the aquo salt with oxygen the alpha salt is not obtained, but instead a totally different substance having the formula $K_2RuCl_5.K_2RuCl_5OH$.

Finally, I would stress the following conclusions at which I arrived after a careful and protracted investigation of the potassium chlororutheniates.

1. No deductions with regard to the formula of any individual preparation can be drawn with safety unless *every* constituent is directly estimated during the analysis. It is quite useless to determine one or two constituents only.

2. Water cannot be determined by merely heating the compounds. The only satisfactory method is to determine hydrogen by combustion over lead chromate in an atmosphere of oxygen. If air is used the results obtained are liable to be too low.

Addendum

Owing to the kindness of the Editor, I have had an opportunity of reading the Note by Professor Howe, which follows.

If the compound formulated as K_2RuCl_5 had a binuclear complex as in the formula $K_4(Cl_4RuCl_2RuCl_4)$, the coördination number of the ruthenium would be six. A formula can also be devised with coördination number eight, the complex being quadrinuclear with four ruthenium ions in a ring, each pair of ruthenium ions sharing three chloride ions. At present we have no knowledge of the actual molecular weight of the compound.

It would appear from Professor Howe's references to the water content of his preparations that there are at least two "aquo"-salts in accordance with the suggestions made in my paper. If his preparations have consisted chiefly or entirely of the compound $K_2RuCl_5.H_2O$, whereas mine were

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[4] Charonnat, *Compt. rend.*, **180**, 1271 (1925).

[5] Miolati and Tagiuri, *Gazz. chim. ital.*, **30**, II, 511 (1900).

[6] Gutbier, Falco and Vogt, *Z. anorg. Chem.*, **115**, 225 (1921).

certainly $2K_2RuCl_5.3H_2O$, the difference in behavior on chlorination might possibly be explained.

BIRSTALL, NR. LEEDS, ENGLAND S. H. C. BRIGGS

RECEIVED MARCH 3, 1926
PUBLISHED AUGUST 5, 1926

The Isomeric Ruthenium Chlorides.—The statement in the recent paper of Howe and Haynes[1] that "Briggs considers that the normal alpha salt is a monohydrate, $K_2RuCl_5.H_2O$, in which the ruthenium has a coördination number of 6," was based on a misunderstanding of his paper. He there states:[2] "It is evident that the coördination number of ruthenium is greater than 6 in the compound $2K_2RuCl_5.3H_2O$." It was wrongly assumed that in $K_2RuCl_5.H_2O$ he considered the number to be 6, as would naturally be expected. There is no reason for assuming a higher coördination number for ruthenium in this compound. On the other hand, the anhydrous form, K_2RuCl_5, which seems undoubtedly to exist, would call for a coördination number of 5.

With Briggs' conclusion that "no deductions with regard to the formula of any individual preparation can be drawn with safety unless *every* constituent is directly estimated during analysis," I should heartily agree, if the sentence were qualified by writing it "no *complete* deduction." In practically all of our recent analyses of the halo-ruthenium salts, we have heated the salt in hydrogen, recovering the evolved halogen in silver nitrate solution. Thus, for example, in the analysis of $K_2RuCl_5.H_2O$ ("aquo" salt), 2KCl + Ru is left in the boat, and Cl_3 collected as silver chloride. There can be no more water than is indicated by loss, and as this has in no case amounted to $1^1/_2$ H_2O, we have been unable to accept Briggs' formula, $2K_2RuCl_5.3H_2O$, for the "aquo" salt.

CONTRIBUTION FROM
WASHINGTON AND LEE UNIVERSITY
LEXINGTON, VIRGINIA
JAS. LEWIS HOWE

RECEIVED MARCH 23, 1926
PUBLISHED AUGUST 5, 1926

The Reaction between Selenium Tetrachloride and Copper.—The reactions between the chlorides of selenium and copper are comparatively much simpler than those between the oxychloride and the same metal.[1] We have determined the course of the reactions both with the monochloride and with the tetrachloride, by analysis. Our results with the former compound agree with those obtained about the same time by Lenher and Kao.[2] On account of qualitative observations we consider that the reaction probably proceeds according to Equations 3 and 4 below.

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[1] Howe and Haynes, THIS JOURNAL, 47, 2920 (1925).

[2] Briggs, *J. Chem. Soc.*, 127, 1042 (1925).

[1] Ray, THIS JOURNAL, 45, 2090 (1923).

[2] Lenher and Kao, *ibid.*, 48, 1550 (1926).

Selenium tetrachloride, made in the usual manner from selenium kindly supplied by the Baltimore Copper Company, was transferred to a bulb at the bottom of a glass tube. This was then bent at an obtuse angle, a weighed roll of freshly reduced copper gauze was introduced, the whole was evacuated through a tube containing phosphorus pentoxide and sealed to the pump. It was then heated for some hours at 105°. The selenium tetrachloride disappeared, and was replaced by drops of a brown liquid (the dichloride, Se_2Cl_2); finally these also were absorbed. The copper gauze was ground in a mortar, and the unchanged copper was picked out. Samples of the total product, and of the soluble and insoluble parts of this, were analyzed separately, and the combined copper, selenium and chlorine were compared with the weight of the selenium tetrachloride taken. All checks, for which analytical data are supplied in our complete paper, agree satisfactorily with the equation,

$$SeCl_4 + 4\ Cu = Cu_2Se + 2\ CuCl_2 \qquad (1)$$

Summary.—By combining the qualitative with the quantitative results, we conclude that the reactions proceed in the following stages,

$$2\ SeCl_4 + 3\ Cu = 3\ CuCl_2 + Se_2Cl_2 \qquad (2)$$

$$Se_2Cl_2 + 5\ Cu = 2\ Cu_2Se + CuCl_2 \qquad (3)$$

and with an excess of the chlorides thus

$$2\ Cu_2Se + 4\ Se_2Cl_2 = 4\ CuCl_2 + 10\ Se \qquad (4)$$

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E. B. R. Prideaux
H. G. Pool

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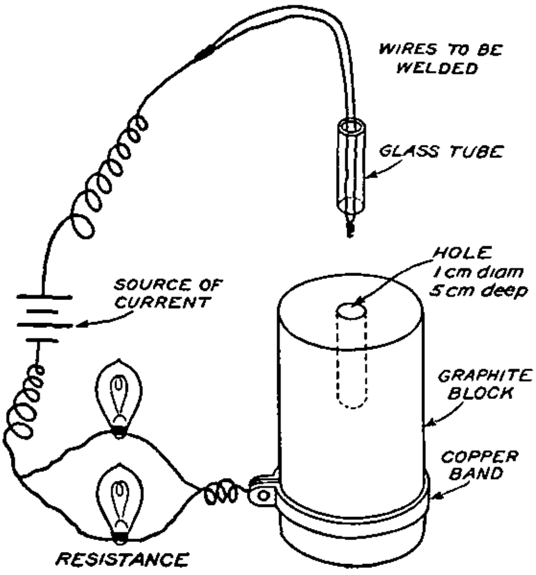
Published August 5, 1926

A Device for Arc-Welding Easily Oxidizable Wires.—I have found the following device very serviceable in welding thermocouples. A hole 1 cm. in diameter and 5 cm. deep is bored in a graphite block. The block forms one terminal and the wires to be welded the other terminal. A drop of "oil-dag," or of common lubricating oil, is dropped into the hole, and the wires are placed in the hole to make a contact with the oil. The wires are then quickly pulled out a very little and the resulting arc, in a reducing atmosphere, gives a very good weld.



A glass tube, open at both ends, may be slipped over the wires to prevent contact with the block at any other place except the very ends, which are twisted together.

Lamps of suitable resistance are placed in parallel. One ampere with 230 volts is sufficient to weld the common wires employed as thermocouples. However, wires of larger gage may be welded by decreasing the resistance.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

STUDIES RELATING TO ALKYL TIN COMPOUNDS. I. SOME STANNOETHANES. II. TRIMETHYLBENZYL STANNANE

BY CHARLES A. KRAUS AND RALPH H. BULLARD[1]

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I. Some Stannoethanes

Introduction.—The elements of the fourth group of the periodic system (not including titanium) form compounds of the type $R_3M.MR_3$, where M is an element of the fourth group and R is an organic group or hydrogen. In these compounds the stability of the bond between the atoms of the element M depends upon the nature of the central element as well as upon that of the substituent groups R. In general, the more electronegative the central element M, the more stable is the bond between the atoms of that element. Thus, tin atoms are bonded much more loosely than are atoms of germanium or silicon. The bond between carbon atoms is extremely stable with the exception of compounds in which the substituents R are aryl or very heavy alkyl groups. The stability of a bond between two carbon atoms in these compounds is the weaker the heavier the substituent groups.

In the case of carbon, these compounds are spoken of as methyls as, for example, triphenylmethyl, the idea being that these compounds consist actually of the free substituted methyl groups. Here there is an attempt to differentiate between the C—C bond as it occurs in the methyls on the one hand and carbon-chain compounds on the other. Such differentiation appears somewhat arbitrary, particularly in the case of other elements of the fourth group, such as lead, tin, germanium and silicon. Little is known with regard to the stability of the Pb—Pb bond. In the case of tin compounds, the Sn—Sn bond is fairly stable, particularly when phenyl groups are the substituents. The Ge—Ge bond appears to be very stable. Probably the stability of the Si—Si bond is even higher than that of germanium.

In view of the gradation in the strength of the bonds of the type M—M

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in the case of the elements of the fourth group, it is not possible to draw a sharp line of distinction between true chain compounds and free radicals such as triphenylmethyl. It appears logical, therefore, to classify these compounds as chains rather than as unsaturated groups. While it is true that, under suitable conditions, certain of these compounds dissociate into their constituent radicals in varying degree, we cannot well utilize this property as a basis for a system of classification.

The free valences of the groups are, in fact, mutually satisfied. The tendency for groups of this type to combine is strictly analogous to that of the atoms of the electronegative elements to polymerize in the free state. While, for example, iodine is dissociated into its atoms at higher temperatures, under ordinary conditions it exists in the dimolecular form in the vapor state and in solution it may have even more complex molecules.

It is an interesting fact that in the case of tin the Sn—Sn bond is much more stable when the substituents are aryl than when they are alkyl groups. In the case of carbon the reverse is true. It seems not unlikely that steric hindrance is involved here. It might be expected that such effects would play a diminishing role as the effective area of the atom increased.

The present investigation was undertaken for the purpose of preparing a number of compounds involving the Sn—Sn bond and gaining some notion with regard to their stability.

A number of compounds of the type $R_3'Sn{\cdot}SnR_3''$ have been prepared in the present investigation and it has been shown that in benzene at higher temperatures these compounds undergo reaction with the formation of the compounds $(R'_3Sn)_2$ and $(R''_3Sn)_2$. Incidentally, compounds between groups containing different substituents may be made according to two distinct reactions, namely

$$R'_3SnNa + BrSnR''_3 = NaBr + R'_3Sn{\cdot}SnR''_3 \qquad (1)$$

$$R''_3SnNa + BrSnR'_3 = NaBr + R''_3Sn{\cdot}SnR'_3 \qquad (2)$$

The two reactions lead to the formation of the same compound but it is of interest to note that, in the case of reactions involving the trimethyltin and triphenyltin groups, one proceeds quantitatively while the other leads to a mixture of stannoethanes.

Hexamethyl Stannoethane, $(CH_3)_3Sn{\cdot}Sn(CH_3)_3$.—This compound was prepared according to the method of Kraus and Sessions[2] by the reduction of trimethyltin bromide with sodium in liquid ammonia.

Since hexamethyl stannoethane is appreciably volatilized by ammonia vapor, the supernatant solvent layer was siphoned off when the reaction was completed. The stannoethane was then washed with water, separated from the water layer and dried by filtering through sodium sulfate in an atmosphere of nitrogen. Finally, the liquid was transferred to small weighed tubes in an atmosphere of nitrogen and sealed; yield 84% of pure material.

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[2] Kraus and Sessions, THIS JOURNAL, 47, 2361 (1925).

Anal. Subs., 0.5260 g.: SnO_2, 0.4833. Calcd. for $[(CH_3)_3Sn]_2$: Sn, 72.48. Found: 72.37.

Mol. wt. Subs., 0.3268, 0.6592; in benzene, 22.28, 22.28: Δt, 0.225, 0.450. Calcd. for $[(CH_3)_3Sn]_2$: mol. wt., 327.6. *Found: 326.0, 328.7, av., 327.4.*

These results show clearly that even at fairly low concentrations trimethyltin exists in benzene near its freezing point in the dimolecular form.

Trimethyltriethyl Stannoethane, $(CH_3)_3Sn \cdot Sn(C_2H_5)_3$.—This compound was prepared according to Reactions 1 and 2. It is a liquid at ordinary temperatures and the method of manipulation was identical with that used in the case of hexamethyl stannoethane.

So far as could be determined, the products of Reactions 1 and 2 were identical. Compounds of this type are so difficultly volatile that no test of identity is possible by comparison of their boiling points. Both products remained liquid at temperatures as low as —60°. That the product of this reaction did not consist of a mixture of hexamethyl and hexa-ethyl stannoethanes was shown by comparing the properties of the compound with those of mixtures of the two stannoethanes. Hexamethyl stannoethane melts at 23.3° and, according to Sessions[3] and Towne,[4] hexa-ethyl stannoethane is liquid at the temperature of boiling ammonia. In the present investigation, it failed to solidify at —75°. According to Towne,[4] the melting point of hexamethyl stannoethane is lowered on addition of the corresponding ethyl derivative. While Towne's melting-point curve is incomplete, it is clear from his observations that these two stannoethanes form neither compounds nor solid solutions. In view of the very low melting point of the ethyl derivative, the eutectic evidently lies very near to the axis of the methyl compound at a temperature somewhere below —75°. Towne found that in an equimolecular mixture of the two stannoethanes, crystals of hexamethyl stannoethane appear at about —5°. In the present investigation a mixture containing 49.62 mole % of hexamethyl stannoethane and 50.38 mole % of hexa-ethyl stannoethane was found to precipitate crystals of the first compound at —5° which, on warming, disappeared at —3.5°. At —33°a large fraction of the methyltin derivative was precipitated from solution. In view of the fact that the products obtained by Reactions 1 and 2 showed no signs of a solid precipitate at temperatures as low as —60°, we must conclude that the product of the two reactions is a compound between the trimethyltin and triethyltin groups.

Since hexamethyl and hexa-ethyl stannoethane, according to Kraus and Sessions[2] and Rügheimer,[5] are dissociated in benzene at its boiling point, it was to be expected that, if a mixture of these compounds was dissolved in benzene at higher temperatures, reaction would occur with the

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[3] Sessions, Dissertation, Clark University, 1924.

[4] Towne, Thesis, Clark University, 1924.

[5] Rügheimer, *Ann.*, **364**, 53 (1910).

formation of a compound between the trimethyl- and triethyltin groups. To test this point, a mixture containing 44.98 mole % of the former and 50.12 mole % of the latter compound was dissolved in benzene and the solution was concentrated by boiling for 17 minutes, after which the last traces of benzene were removed with a high-vacuum pump. On cooling the resulting product, crystals appeared at —20° which, on slowly warming, disappeared at —19.1°. Since in the original mixture the solid phase (hexamethyl stannoethane) disappeared at —3.5°, it follows that reaction must have taken place in boiling benzene. It may be stated in this connection that the properties of the original pure compounds are uninfluenced as a result of solution in benzene; the pure liquid mixture retains its original properties after standing for some months.

Triphenyltrimethyl Stannoethane, $(C_6H_5)_3Sn{\cdot}Sn(CH_3)_3$.—This compound was prepared according to Reactions 1 and 2.

On treating sodium triphenyltin with trimethyltin bromide in liquid ammonia, a solid was immediately precipitated. This product was repeatedly washed with ammonia, after which the last traces of ammonia were removed with a pump. The final product melted rather sharply to a clear, colorless liquid at 106°. It showed no tendency to oxidize in air.

Anal. Subs., 0.2299, 0.3186: SnO_2, 0.1345, 0.1863. Calcd. for $(C_6H_5)_3Sn_2(CH_3)_3$: Sn, 46.24. Found: 46.09, 46.05.

Mol. wt. Subs., 1.1411, 1.9080; in benzene, 28.038, 28.038: Δt, 0.398, 0.666. Calcd. for $(C_6H_5)_3Sn_2(CH_3)_3$: mol. wt., 513.4. Found: 511.3, 511.0, av., 511.2.

In preparing the material by washing with liquid ammonia, practically no tin was carried over with the washings. In other words, the only product removed in this process is sodium bromide. Since the product was not otherwise purified and since the melting point of the product was sharp, the inference is that the reaction as carried out proceeded quantitatively.

A reaction was also carried out between sodium trimethyltin and triphenyltin bromide in liquid ammonia. A precipitate was immediately formed on introduction of the bromide. After washing with liquid ammonia, the product failed to yield a definite melting point. In most instances it began to soften at about 100°, but the solid did not completely disappear until a temperature of 150° or more was reached. This result suggested that the reaction, in this case, did not proceed quantitatively with the formation of triphenyltrimethyl stannoethane. Presumably hexamethyl and hexaphenyl stannoethane were also formed.

On dissolving the product of this reaction in ether and carrying out a series of recrystallizations, a compound was finally obtained which melted at 103°. From the residue was obtained a compound melting at 223–225°. This appeared to be impure hexaphenyl stannoethane, whose melting point is 232°.

A mixture of the product of the first reaction with the purified product of the second reaction showed the same melting point as the constituent materials. This shows that in the main the second reaction leads to the same product as the first, but while the first proceeds quantitatively, the second does not. Evidently the course of the reaction depends, in a measure, on the sign of the charge on the two groups. It is interesting to note that while trimethyltin is readily oxidized, the compound between the trimethyltin and triphenyltin groups is stable with respect to oxygen. In this respect it resembles hexaphenyl stannoethane.

II. Trimethylbenzyl Stannane, $(CH_3)_3Sn{\cdot}CH_2{\cdot}C_6H_5$

Preparation.—Sodium trimethyl stannide was treated with an equivalent quantity of benzyl chloride in liquid ammonia. Reaction takes place according to the equation

$$(CH_3)_3SnNa + C_7H_7Cl = (CH_3)_3SnC_7H_7 + NaCl \qquad (3)$$

The compound is precipitated in the form of fine drops which coalesce on stirring. This liquid was washed with water, filtered and dried. It cannot be purified readily by distillation since it decomposes when heated to 215°. The reaction proceeds quantitatively and the product obtained appeared to be quite pure.

Anal. Subs., 0 4337: SnO_2, 0.2308. Calcd. for $(CH_3)_3SnC_7H_7$: Sn, 46 60. Found: 46 56.

Mol. wt. Subs., 0 5655, 1.0157; in benzene, 23.189, 23.189: Δt, 0.4715, 0.875. Calcd. for $(CH_3)_3SnC_7H_7$: mol. wt., 254.7. Found: 258.6, 250.3, av., 254.6.

Bromination of Trimethylbenzyl Tin.—According to Grüttner and Krause,[6] when a quaternary organic tin compound is brominated at low temperatures, the lightest group is substituted. An attempt was made to carry out such bromination in the case of the monobenzyl derivative. It was found that the benzyl rather than a methyl group is replaced on bromination.

A weighed quantity of trimethylbenzyl tin was dissolved in ether and to this was added the equivalent quantity of bromine dissolved in ether, the solution being cooled to liquid ammonia temperatures. This method is recommended by Grüttner and Krause.[7] After evaporation of the ether the resulting product was distilled, the distillate coming over between 174° and 200° being collected. Such change of boiling point, alone, shows that the reaction did not proceed as was expected.

Mol. wt. Subs., 0.6057, 1.1372; in benzene, 23.786, 23.786: Δt, 0.637, 1.172. Calcd. for $(CH_3)_3SnBr + C_7H_7Br$: mol. wt., 208. Found: 199.9, 204 0, av., 202.0.

According to molecular-weight determinations, then, the product obtained on brominating trimethylbenzyl tin consists of a mixture of trimethyl tin bromide and benzyl bromide in equimolar proportions. Apparently in this instance the heavier rather than the lighter group is substituted on bromination.

Summary

1. The molecular weight of hexamethyl stannoethane in benzene by the cryoscopic method corresponds to the formula $[(CH_3)_3Sn]_2$.

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[6] Grüttner and Krause, (a) *Ber.*, 49, 1128 (1916); (b) 50, 203, (c) 1804 (1917).

[7] Ref. 6 a, p. 1419. Ref. 6 c.

2. An equimolecular liquid mixture of hexamethyl and hexa-ethyl stannoethane is in equilibrium with solid hexamethyl stannoethane at —3.5°. A mixture of the two compounds in boiling benzene solution gives evidence of interaction between the trimethyl- and triethylstannyl groups.

3. The mixed stannoethanes, $(CH_3)_3Sn{\cdot}Sn(C_2H_5)_3$ and $(CH_3)_3Sn{\cdot}Sn(C_6H_5)_3$, have been prepared and some of their properties studied. The compounds were prepared by two reactions in which the charges on the interacting groups were, respectively, reversed. The same compounds were formed in the two cases, but one reaction in the case of the phenyl derivative led to the formation of the pure compound and the other to a mixture of this compound with hexamethyl and hexaphenyl stannoethanes.

4. Trimethylbenzyl tin has been prepared. On brominating this compound in ether solution at liquid ammonia temperatures, the benzyl group is substituted.

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[CONTRIBUTION FROM THE PROTEIN INVESTIGATION LABORATORY, BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE ROLE OF THE PROTEOLYTIC ENZYMES IN THE DECOMPOSITION OF THE HERRING[1]

BY L. H. ALMY

RECEIVED DECEMBER 17, 1925 PUBLISHED AUGUST 5, 1926

The immature herring, *Clupea harengus*, is canned as the sardine in Maine. According to the usual procedure, the fish are caught in weirs, transferred to the hold of the sardine boat, treated there with salt, and transported to the factory, where they are washed, held in brine for one to two hours, removed therefrom and steamed for ten or fifteen minutes, dried somewhat in a current of warm air, and packed in cans. Mustard or oil is added, and the cans are capped, sealed and processed.[2]

Ordinarily the fish decompose very little before they are canned, as the interval between their removal from the water and their steaming is comparatively short. When caught, the fish are usually in search of food; occasionally a large proportion of the herring taken from a weir have feed in their digestive tracts. Such "feedy" fish decompose rapidly, and

[1] The author wishes to acknowledge his indebtedness to the Biological Board of Canada for permission to use the facilities of the Atlantic Biological Station, St. Andrews, N. B., to Professor A. G. Huntsman, Director of the Station, and his Staff, for valuable assistance rendered in the course of the study, and to R. M. Hann of the Bureau of Chemistry, U. S. Department of Agriculture, for electrometric measurements of the hydrogen-ion concentration of buffered solutions.

[2] For details of the canning process see Weber, "The Maine Sardine Industry," *U. S. Dept. of Agriculture Bull.*, No. 908 (1921).

yield a canned product of poor quality. The ventral tissues soften quickly, and, if not already torn, the abdominal wall is ruptured during the steaming process. The appearance of such fish suggests an explosive bursting. These breaks are probably caused to a certain degree by the rapid expansion of gas which is often found in the stomach of feedy fish.

According to Obst,[3] bacteria are responsible for the decomposition of the herring which contain undigested food residues in the alimentary tract. On the other hand, the digestive tract of non-feedy fish was usually sterile. Obst isolated two organisms from the natural feed of the herring (crustacean forms, that is, copepods and schizopods) and from the stomach contents of the fish. Both of the organisms isolated were anaërobes and produced gas when grown in suitable culture media at 37°. The gas in the stomachs of feedy fish was believed to have resulted from the action of these organisms on the feed. Weber and Wilson[4] concur with Obst in the opinion that the decomposition of feedy fish is due to the action of these bacteria. They base this conclusion on their observation that ammonia and amines are formed in abundance during the decomposition of the feed and also by the action of the isolated bacteria on a dextrose and fish-flesh medium. It is apparent that the evidence submitted in favor of this view is largely circumstantial.

Feedy herring decompose much more rapidly than would be expected from the action of the relatively small numbers of bacteria present. Linden[5] believed that bacteria take only a secondary part in spoilage of this type. The present paper reports a study of the proteolytic enzymes of the herring from the standpoint of the part they may play in the deterioration of feedy fish.

Numerous studies on the enzymes of fish reported in the literature[6] show that the proteolytic enzymes of fish are more active at temperatures of 37° to 40° than at lower temperatures and that the optimum hydrogen-ion concentrations for their action appear to be about the same as those for the corresponding mammalian enzymes. Very little exact work on this phase of the subject, however, has come to the attention of the author.

The stomach of the herring consists of two sacs, the larger, the cardiac sac, extending straight back from the esophagus, and the smaller, the pyloric sac, branching off from the junction of the esophagus and cardiac sac. The posterior end of the cardiac sac communicates with the air

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[3] Obst, *J. Infectious Diseases*, **24**, 158 (1919).

[4] Weber and Wilson, This Journal, **42**, 841 (1920).

[5] Linden, unpublished report, Bureau of Chemistry, U. S. Department of Agriculture.

[6] For reviews of the literature on the enzymes of fish see Sullivan, *U. S. Bur. Fisheries Bull.*, 1908, XXVII, 3, and Biedermann, in Winterstein's "Handbuch der vergleichenden Physiologie," Jena, **1911**, ii, p. 1049. Recent work is discussed by Kenyon, *U. S. Bur. Fisheries Bull.*, **1925**, XLI, 181.

bladder through the pneumatic duct. The lower end of the pyloric sac joins the intestine, at the head of which are attached tubular organs called pyloric ceca. The peptic enzyme is found in both the cardiac and pyloric sacs. The tryptic enzyme is found in the pyloric ceca.[7]

The investigation here reported deals in the main with the relative strengths of the proteolytic enzymes from feedy and non-feedy fish, together with the determination of the temperature coefficient of the tryptic activity, and the autolysis of the flesh of the fish under different conditions.

The digestive organs were readily comminuted by grinding in a mortar with sea sand. The extractions were made at 0° to 5° by intermittent mechanical shaking for four hours, using 10 parts of extracting liquid to one part of stomach or cecal tissue. The extracts were filtered in the cold. When water was used as the extracting fluid the filtrate was diluted with an equal volume of glycerol to act as an enzyme preservative.

Pepsin

Tests of the action of the enzyme on fibrin stained with Congo red in buffered solutions of known Sörensen value (*P*H) showed that (a) water is slightly more efficacious than 30% alcohol or 85% glycerol as an extracting medium for the enzyme of the stomach, (b) digestion by the aqueous extract is greater at 37° than at 25° and greater at 25° than at 15° and (c) the aqueous extract is more potent at *P*H 2.5 to 2.85 than at higher or lower hydrogen-ion concentrations.

In comparing the relative strengths of the enzymes from feedy and non-feedy fish, the organs from five fish of uniform size were combined to obtain sufficient material to work with conveniently. For the determination of the enzymic strength of the extracts gelatin was used as the substrate and the rate of hydrolysis was followed by periodic determinations of the viscosity of the solution, using the method devised by Northrop and Hussey.[8] The gelatin employed was electrolyte-free, having been prepared by the procedure recommended by Smith.[9] A 3% gelatin solution was made by soaking the air-dry gelatin in a small quantity of Sörensen's citrate buffer of *P*H 1.95, melting the swollen gelatin mixture by heating for 10 minutes at 60°, and then diluting to the appropriate volume with the buffer solution. The resulting solution had a *P*H of 2.65, which is in the optimum range for the action of the enzyme on fibrin. The viscosity determinations were made in ordinary 2cc. Ostwald viscosity pipets submerged in a water-bath held constant at 37.5 ± 0.05°. Five-tenths cc. of the enzyme solution was added to 25 cc. of gelatin solution, which had previously been held at 37.5° for one hour. After thorough mixing,

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[7] Stirling, *2nd Annual Rept. Fish. Bd. Scotland,* **1884,** Appendix F, No. 1, 31.

[8] Northrop and Hussey, *J. Gen. Physiol.,* **5,** 353 (1923).

[9] Smith, This Journal, **43,** 1350 (1921).

5 cc. of the mixture was transferred to the pipet and the viscosity determined immediately and at convenient intervals thereafter during one hour's digestion. Two pipets were used, with each of which the enzymic strengths of the extracts from both feedy and non-feedy fish were tested.

The stomach enzyme in the preliminary tests with fibrin was found to be only very slightly active at *P*H 4.0 and practically inactive at higher *P*H values. The *P*H of the tissue of the abdominal wall of the herring was found by the colorimetric method, using Clark's indicators, to be between *P*H 6.2 and *P*H 6.6, a range outside of the effective range for the activity of the peptic enzyme. The curves in Fig. 1 show that less enzyme is extractable from the stomach of feedy fish than from the stomach of non-feedy fish, whether the stomach and contents or only the stomach tissue is extracted. The evidence is, therefore, against the supposition that the stomach enzymes are concerned in the rapid decomposition of feedy fish.

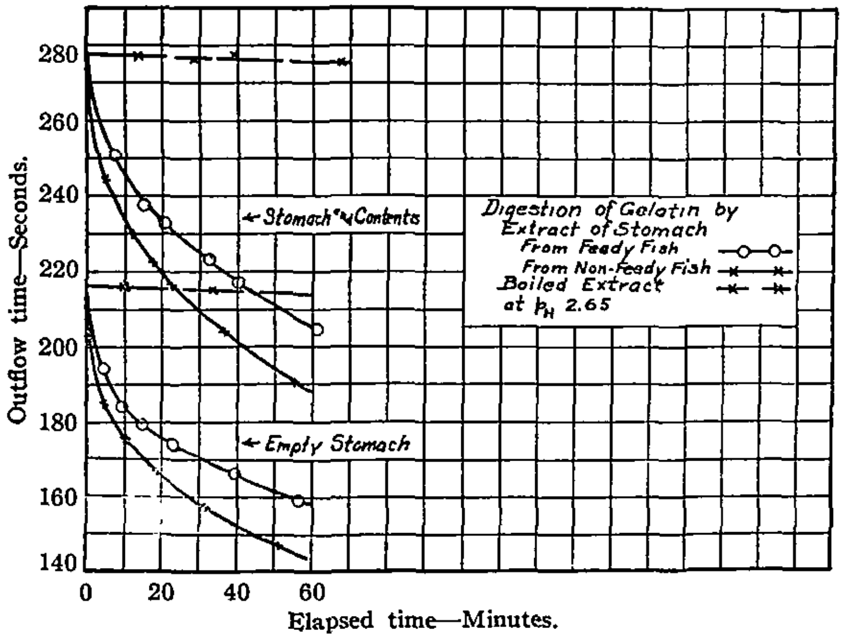

Fig. 1.

Trypsin

Again using fibrin, the aqueous extract of the pyloric ceca was found to be most active at blood heat and at approximately *P*H 9.0 ± 0.5. The enzymic strength was then determined as before with gelatin as the substrate. A 3% gelatin solution was prepared as previously described, except that solution was effected with Sörensen's borate buffer to yield a final value of *P*H 8.76. As the trypsin solution was much more active than the corresponding pepsin solution, it was necessary to dilute the cecal extract with four volumes of 1:1 glycerol solution before testing in order to procure a rate curve comparable with that obtained with the stomach extract.

The tryptic enzyme in the tests with fibrin was found to be active at *P*H 6.85, that is, near the range of the Sörensen value of the flesh of the abdominal wall. The action, however, was slight compared with that at the optimum hydrogen-ion concentration. As the ceca are adjacent to the ventral wall, it is reasonable to suppose that the enzyme of the pyloric ceca may play some part in the decomposition of feedy fish. Furthermore, the ceca of the feedy fish appeared to be congested and easily ruptured compared with those of the non-feedy fish. The curves in Fig. 2 show that the extract of the ceca of feedy fish is more active or stronger than that of the ceca of non-feedy fish. These results were confirmed by tests on three lots of fish of both types. Considered in connection with the condition and location of the ceca, they seem to point to the enzymes of this organ as the cause for the rapid decomposition of the body wall of feedy herring.

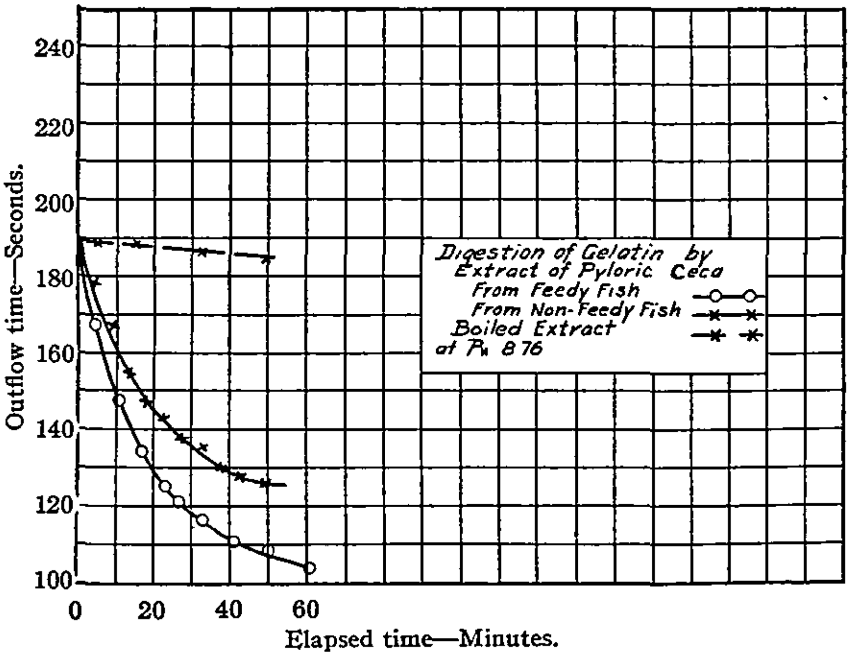

Fig. 2.

Temperature Coefficient of Trypsin.—As the temperature of the herring seldom rises above 20° from the time they are removed from the water until they are placed in the steam chest of the cannery, it is apparent that the proteolytic enzyme of the ceca must be active at comparatively low temperatures if it is to produce any appreciable change. Working with mammalian trypsin, Ramsey[10] found that for "the tempera-

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[10] Ramsey, "Temperature Coefficients of Enzyme Activity and the Heat Destruction of Trypsin," *Dissertation*, Columbia University, 1925.

ture range where the destruction of the enzyme does not play an important part the rate of hydrolysis is about doubled for a rise of ten degrees in temperature." Using casein as the substrate and following the method essentially as outlined by Sherman and Neun,[11] the effect of temperatures on the activity of the tryptic enzyme from the herring was studied. The amino-acid nitrogen of the digested casein was determined by the Sörensen titration method, the results being expressed in terms of 0.2 *N* sodium hydroxide solution. The results (Fig. 3) indicate that for every 10° rise the activity of the enzyme is increased not more than 50%, corresponding to a temperature coefficient of 1.5. This fish enzyme, therefore, is relatively more active at the lower temperatures than the corresponding mammalian enzyme, a fact which is in harmony with the idea that the enzyme is responsible for the breaking down of the tissues of feedy fish at the comparatively low temperature range of 10° to 20°.

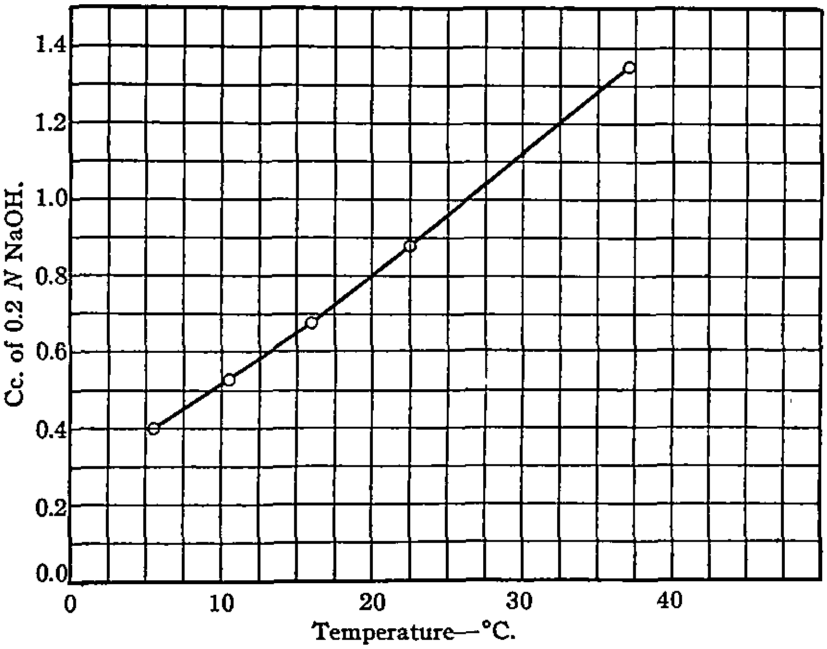

Fig. 3.—Digestion of casein by extract of pyloric ceca at different temperatures; 14 hours' incubation.

Autolysis[12]

According to Chen and Bradley,[13] the muscle tissue of vigorous swimming fish appears to autolyze more extensively than that of sluggish swimming

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[11] Sherman and Neun, THIS JOURNAL, 38, 2199 (1916).

[12] As ordinarily used, the term "autolysis" means digestion of a tissue by the enzymes in the cells themselves. It is here used to cover digestion of a mixture by any enzymes that may be present in one or more constituents.

[13] Chen and Bradley, *J. Biol. Chem.*, 59, 151 (1924).

fish. If this conclusion is correct, the rate of autolysis of the flesh of the herring, which may be considered an active fish, should be comparatively high. A number of experiments were performed to determine the part played by muscle autolysis in the decomposition of feedy herring and the influence of different organs on the enzymic digestion of the muscle proteins. The method of Bradley and Taylor,[14] with slight modification, was used. The mid-section of the fish was obtained by cutting off the head just back of the gill cover and the tail at the anus. The entrails were removed, and the remaining tissues consisting of the muscle tissue, bones, skin and dorsal fin, were ground twice in a meat chopper, with and without the addition of various internal organs. Two parts of this material, together with 7 parts of water and 1 part of toluene, were placed in a pint (500 cc.) fruit jar. The mixture was thoroughly shaken and held for a few days at 37° or at room temperature. In the beginning and at intervals, 25cc. portions measured in a graduated cylinder were transferred to 100cc. volumetric flasks and treated with 50 cc. of 5% trichloro-acetic acid solution. The mixture after being shaken was diluted to the mark with water. Twenty-five cc. of the filtrate therefrom was titrated by the formol method, the results being expressed in the tables in terms of cubic centimeters of 0.2 *N* sodium hydroxide solution per 25 cc. of filtrate.

Table I

Autolysis of Herring at 37°

			0.2 *N* amino acids, cc.				
Expt.	Mixture	Days 0	1	2	3	7	14
I	Flesh of feedy fish..................	0.45	0.65	0.70	..	...	1.00
	Flesh of non-feedy fish..............	.45	.65	.60	..	...	1.00
II	Flesh and entrails of feedy fish.......	.45	5.40	6.90	7.90	...	..
	Flesh and entrails of non-feedy fish....	.45	1.70	2.55	3.80	...	..
III	Flesh and entrails (except stomach) of feedy fish......................	.60	4.15	5.40	7.10	...	..
	Flesh and entrails (except stomach) of non-feedy fish...................	.50	2.05	3.40	5.25	...	..
IV	Flesh and entrails (except ceca and intestines) of feedy fish.............	.50	1.10	1.40	1.70	...	..
	Flesh and entrails (except ceca and intestines) of non-feedy fish..........	.50	0.90	1.05	1.20	...	..
V	Flesh and stomach of feedy fish.......	.60	.90	1.20	..	...	..
	Flesh and stomach of non-feedy fish...	.50	.85	0.95	..	...	.
VI	Flesh and ceca of feedy fish..........	.50	3.90	5.70	..	7.4	..
	Flesh and ceca of non-feedy fish......	.45	1.60	3.40	..	6.1	..
VII	Flesh and intestines of feedy fish......	.55	0.75	1.00	..	...	..
	Flesh and intestines of non-feedy fish...	.50	.80	1.10	..	...	..

Table I shows that marked decomposition occurred only in the mixtures containing the pyloric ceca (Expts. II, III and VI). Similar results were obtained when the mixtures were incubated at 17° to 18°. The autolysis

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[14] Bradley and Taylor, *J. Biol. Chem.*, 25, 261 (1916).

of the muscle tissue (Expt. I) plays a comparatively insignificant part in the breaking down of the muscle proteins, and the stomach and intestines (Expts. V and VII) are likewise relatively inactive. It is apparent that the ceca of feedy fish produce a much greater change than those of the non-feedy fish.

When the crustacea are plentiful the herring gorges itself with food and the cardiac sac of the stomach of feedy fish is usually distended to several times its size when empty. The resultant crowding of the other organs causes a pressure of the ceca against the abdominal wall. The fish in the lower layers in the holds of the sardine boats and in the pickling vats in the cannery are subjected to the pressure of the upper layers. The external and internal pressure and numerous handlings, coupled with the fact that the ceca of feedy fish are congested and readily ruptured, offer a condition favorable to the diffusion of the tryptic enzyme from the ceca into the tissues of the body wall. That diffusion actually occurs was demonstrated by experiment. Feedy and non-feedy fish were held for eight hours at approximately 20°. The abdominal wall was then excised and carefully cleaned to remove any adhering organ tissue. When allowed to autolyze as in the previous experiments, the results, similarly expressed, for 0, 1 and 3-day incubation at 37°, were as follows: feedy fish, 0.6 cc., 1.60 cc. and 3.90 cc.; non-feedy fish, 0.50 cc., 0.60 cc. and 0.90 cc. Enough of the enzyme had penetrated the tissues of the feedy fish to cause a rapid hydrolysis of the proteins.

As the alimentary tract of feedy herring contains bacteria and that of the non-feedy fish is usually sterile,[3] it might be conjectured that bacteria as well as enzymes would play a part in the decomposition of the feedy fish. The experiments reported in Table II show that during incubation for eight hours at 37° bacteria are apparently not concerned in the decomposition of non-feedy fish, but do assist in the decomposition of feedy fish. That putrefactive bacteria are present in the feed of the herring is shown

TABLE II

DECOMPOSITION OF HERRING AT 37° WITH AND WITHOUT TOLUENE AS PRESERVATIVE

		0.2 N amino acids, cc.				
Expt.	Mixture	Hours 0	5	8	24	48
VIII	Flesh and entrails of feedy fish, no preservative	0.50	3.5	5.0	...	..
	Flesh and entrails of feedy fish, with toluene	.50	2.75	3.75	...	..
IX	Flesh and entrails of non-feedy fish, no preservative	.40	0.80	1.00	...	..
	Flesh and entrails of non-feedy fish, with toluene	.40	.70	0.90	...	..
X	Flesh of non-feedy fish and copepods, no preservative	.55	.80	..	3.2	9.80
	Flesh of non-feedy fish and copepods, with toluene	.55	.65	..	1.05	1.50

in Expt. X. For this test live copepods amounting to a volume of 4 cc. were killed by grinding in a mortar with sand, and the finely divided material was added to the usual autolysis mixture containing 50 g. of flesh.

Discussion

It has been shown that the proteolytic enzyme of the stomach is weaker and that of the pyloric ceca is stronger in feedy than in non-feedy fish. A plausible explanation of the former condition is that part of the peptic enzyme has been fixed by the food present and part has been eliminated through the intestine, leaving only a fractional part of that which was originally stored. Apparently the enzyme is formed more slowly than it is eliminated from the field of action.

In view of the large quantity of trypsin demonstrable in the pyloric ceca, it may reasonably be assumed that this organ secretes the enzyme. Massed copepods or schizopods appear to be practically white except for the black eyes of the schizopods. During digestion in the alimentary tract of the herring, however, the mass becomes pink or red, a change probably related to the presence of chitinous tissue. It was noted that the ceca of non-feedy fish were pale and contracted, whereas those of feedy fish were of the same color as the partially digested crustacea and somewhat swollen. It is judged from this that some at least of the liquid food residues leaving the stomach enter the ceca, undergo further digestion and are probably absorbed there. The appearance of the pyloric ceca of feedy king salmon as described by Greene[15] agrees with that observed by the author in the herring. Greene believed that the ceca are the principal organs of absorption of fats in the king salmon.

The tryptic enzyme is probably being formed and actively secreted as long as food residues are present, and the rate of formation would have to be greater than the destruction or elimination to account for the difference in proteolytic activity of the cecal extract of feedy and non-feedy fish. Other factors may enter into this, however. The presence of food in the stomach, before and after it has reached the ceca, may induce the formation and secretion of the enzyme in the ceca, thus building up a supply which, during subsequent digestion, is never depleted to the predigestion level. Furthermore, the mineral salts in the food, particularly the calcium salts, may increase the activity of the trypsin. The catalytic effect of calcium salts on the activity of the cecal extract of non-feedy fish was not studied.

The rapid decomposition of feedy herring has been shown to be largely enzymic. The data also show, however, that bacteria may play a part. Micro-organisms are present not only in the digestive tract of feedy fish, but also on the gills. The fecal material eliminated by the fish voluntarily or mechanically contains large numbers of bacteria. It can readily

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[15] Greene, *Bur. Fisheries Bull.*, 33, 153 (1913).

be seen that there is the possibility that practically all of a lot of mixed feedy and non-feedy fish piled in the hold of a sardine boat would become infected through the exterior surface.

In reference to the possibility of the penetration of bacteria into the muscular tissue of the abdominal wall from the intestine, perhaps one could not do better than to quote Anderson:[16] "One frequently finds, especially in dealing with herring or cod, some whose stomachs were evidently packed with crustaceans or small fish at time of capture, and in these cases digestion and solution of the wall of gut may take place in a few hours, whereas if the gut is comparatively empty the digestion may be considerably delayed. This certainly takes place very rapidly in herring in the above condition......But when one has due regard to the rapidity in many cases with which solution of the gut wall takes place, it appears to be at least initiated by *post-mortem* digestion, although this process may be accompanied by, and is certainly soon superseded by, the action of bacteria of putrefaction which abounds in the gut... ..I have frequently found *bacillus coli* (in the peritoneal fluid[17]) in about 45 to 60 minutes after death, and in a very few cases even 30 minutes after death. After one hour they will be found readily in greatly increasing numbers." The rapid disintegration of the tissues of the ventral wall of the immature feedy herring resulting from the action of the enzyme of the pyloric ceca makes possible the ready penetration of the bacteria from the peritoneal cavity. It is apparent, therefore, that under the conditions obtaining in the sardine industry when feedy fish are used the flesh is subject to infection by bacteria which may gain entrance through both the outer integument and the peritoneum. The visible evidence of decomposition—the softening and bursting of the abdominal wall—is, however, practically wholly an enzymic manifestation.

The gas often found in the posterior end of the cardiac stomach of feedy fish, the rapid expansion of which during the steaming process appears to be the cause of the bursting of the stomach and abdominal walls, is believed by Obst[3] (but not proved) to have its origin in the action of gas-producing anaërobic bacteria present in the feed. Attention should be called, however, to the fact that this sac communicates with the air bladder through the pneumatic duct and it is not impossible that, owing to the paroxysms accompanying death by asphyxiation and also perhaps to pressure on the air bladder during subsequent handling, gas from the bladder gains entrance to the stomach and becomes locked therein. Consideration of this possibility raises a reasonable doubt as to the correctness of the theory that the gas results wholly from the action of bacteria.

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[16] Anderson, *26th Annual Rept. Fish. Bd. Scotland,* 1907, Part III, Sci. Investigations, 13.

[17] Inserted by the author.

Summary

A biochemical investigation on the immature herring (used in sardine packing) to determine the cause of the decomposition of feedy fish, which makes them unacceptable for food purposes within a few hours, showed the following points.

1. The pepsin extracted with water from the stomach of the fish is more active at 37° than at lower temperatures and at hydrogen-ion concentrations between *P*H 2.5 and *P*H 2.85 than at higher or lower values. It is comparatively inactive above *P*H 4.0. Less pepsin is extractable from the stomach of feedy fish than from the stomach of non-feedy fish.

2. The trypsin extracted with water from the pyloric ceca is more active at blood heat than at lower temperatures and between *P*H 8.5 and 9.5 than at higher or lower values. It acts slowly, however, at *P*H 6.85. Decidedly more trypsin is extractable from the ceca of feedy fish than from the ceca of non-feedy fish.

3. In mixtures of ground flesh and digestive organs, enzymic digestion is rapid and is attributable mainly to the presence of the pyloric ceca. The stomach and intestines, as well as muscle autolysis, play only an insignificant part in the breaking down of the proteins.

4. The flesh of feedy fish is invaded by bacteria and by the trypsin of the pyloric ceca, but the visible evidence of decomposition—the softening of the abdominal wall—is due almost solely to the action of the trypsin, which is greater in amount or more active than that in the ceca of non-feedy fish, and which readily escapes from the delicate and highly congested tubules, quickly penetrating to the adjacent tissues of the ventral wall.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY, NEW YORK UNIVERSITY]

THE BASIS FOR THE PHYSIOLOGICAL ACTIVITY OF CERTAIN -ONIUM COMPOUNDS. V. THE MOBILITIES OF THE -ONIUM IONS. II[1]

BY ISAAC BENCOWITZ[2] WITH R. R. RENSHAW

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The problem of determining which properties of the -onium compounds are responsible for their physiological effects has been discussed in some detail elsewhere. It was there pointed out that evidence exists for believing that some sort of an electrical effect[3] is involved. It seems de-

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[1] This problem is being carried on in coöperation with Dr. Reid Hunt of the Harvard Medical School. The physiological data are the basis of a series of papers published elsewhere by him.

[2] National Research Fellow in Chemistry.

[3] Renshaw, *Science*, 62, 384 (1925).

sirable, therefore, to obtain data on the mobilities of several of the -onium ions, including such ions as would give a representative variation in activity. No attempt will be made to discuss relationship of mobilities with muscarine and nicotine effects of these ions until further data are available.

In this, the second paper on the mobilities of -onium ions, data are presented for the mobilities of the tetramethyl-, tetra-ethyl- and tetrapropylammonium ions.

Preparation of Materials

Tetramethylammonium Bromide.—The tetramethylammonium bromide used in this investigation was an Eastman Kodak Company product. It was twice recrystallized from conductivity water, washed with absolute alcohol and dried in a vacuum desiccator over phosphorus pentoxide.

Tetra-ethylammonium Chloride and Tetrapropylammonium Iodide.—These salts were Kahlbaum products. They were purified by recrystallization from alcohol and subsequent washing with ether. The salts were then dried in vacuum desiccators. The tetrapropylammonium iodide was kept in the dark inasmuch as on exposure to light it turned yellow. As an additional precaution, the upper layer was scraped off and discarded; only the white crystals were used in making up the stock solution.

Water.—The water employed in this investigation was prepared by a method developed in this Laboratory.[4] The conductivity of the water used was about 0.1×10^{-6}.

Measuring Apparatus

The bridge assembly, cells and the technique of cleaning and drying the latter have been described in an earlier paper.[5] The large quartz cell was slightly modified in order to avoid any possible error in making up the solutions.

This cell, shown in Fig. 1, consisted of a 1-liter Vitreosil flask A. The electrodes had an area of about 5 sq. cm. and were placed approximately 4 mm. apart. The electrodes were sealed into the quartz tube C. The stock solution was introduced into the cell from a weight pipet through the quartz tube D. The lower end of this tube was below the surface of the solution in the cell; the upper end was connected by means of rubber tubing to a wide glass tube E. The latter contained an inner tube F. When suction was applied to tube F, the solution in the cell was lifted up to the very end of the quartz tube D. This washed out any of the stock solution that might cling to the walls of the tube and cause an error in the concentrations. The water in the tube E formed a seal between the solution and the outside air. A blank test showed that no change in the conductivity took place during the time required to introduce the stock solution into Tube D. This arrangement was found to be very satisfactory. The solution was stirred by a slow current of purified air which had been

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[4] Bencowitz and Hotchkiss, *J. Phys. Chem.*, 29, 705 (1925).

[5] Bencowitz and Renshaw, This Journal, 47, 1904 (1925).

previously saturated and brought to the required temperature. The air was blown into the cell through the quartz tube B. While collecting conductivity water the cell was connected with the still by means of Tube D.

Cell Constants.—Two auxiliary cells previously described by the authors were employed for the purpose of calibrating the quartz cell. The cell constant of Cell I was calibrated with 0.1 *D* (0.1 mole per 1000 cc. of solution) potassium chloride solution made up as directed by Parker and Parker.[6] The cell constant of Cell I determined in May, 1925, and used in this investigation was 2.0807 which checked very closely with the cell constant of 2.0813 and 2.0810 determined on June 7 and October 24, 1924, respectively. It will be seen that there is a general drift in the constant. This was also noticed by Kraus.

Cell II was intercompared with Cell I and the quartz cell was intercompared with Cell II. All precautions recommended by previous investigators[7] and employed by the authors in an earlier paper were closely observed and need not be described here. Suffice it to say that the cell constant of the quartz cell was redetermined after each run.

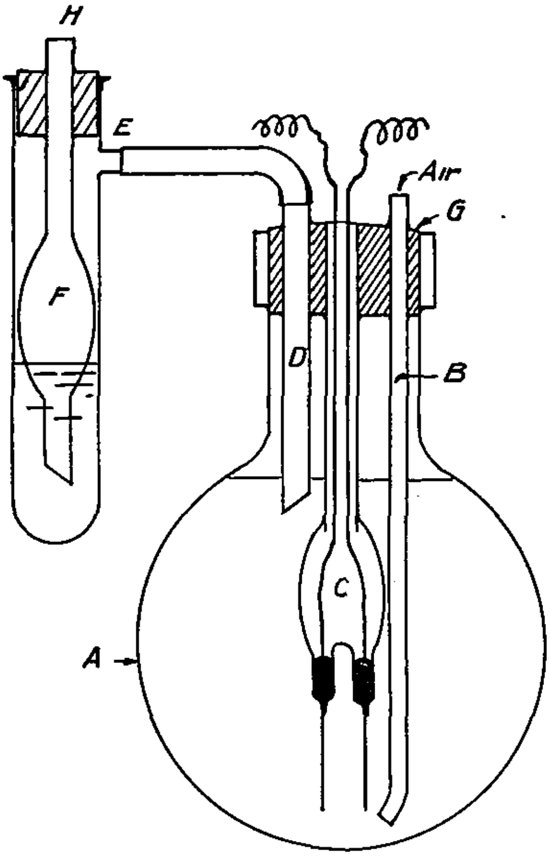

Fig. 1.

TABLE I

CONSTANTS OF QUARTZ CELL USED IN MEASURING THE CONDUCTANCE OF AMMONIUM SALTS

	Tetra-methylammonium bromide	Tetra-ethylammonium chloride	Tetrapropyl-ammonium iodide
Run I	0.029759_8	0.030578_2	0.031985_9
Run II	$.030876_1$	$.033172_9$	$.032117_5$
Run III	$.022715_0$	$.031569_9$	$.032108_0$

Density.—In order to reduce the concentrations to a volume normal basis, it was necessary to determine the density of the salt solution. An

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[6] (a) Parker and Parker, THIS JOURNAL, **46,** 312 (1924). (b) See also Ref. 5.

[7] Kraus and Parker, *ibid.,* **44,** 2429 (1922). Parker, *ibid.,* **45,** 1369 (1923). Morgan and Lammert, *ibid.,* **45,** 1692 (1923). Ref. 5.

Ostwald pycnometer of about 15cc. capacity was employed for the measurements. No fineness in the technique of the density measurement was observed. The experimental error of these measurements, however, is much less than the error with which the concentrations were determined. Furthermore, the corrections for the change in density of dilute solutions employed in this investigation are almost negligible. The densities finally used were read off a smooth curve drawn straight down to the density of water at 25°. For tetraethylammonium chloride the densities of Schiff and Monsacchi[8] were adopted.

Experimental Procedure and Results.—The experimental procedure was very similar to that described in the first paper of this series. The slight changes made were necessitated by the modification of the quartz cell. When the desired quality of conductivity water was collected in the cell, the latter was placed in the thermostat where it was allowed to stand for several hours until temperature equilibrium was reached. This was determined by several resistance measurements. The resistance of the water having been determined, the first concentration was made by introducing a weighed quantity of the stock solution which had been made up previously. This solution was prepared by weighing out carefully a calculated amount of the salt and introducing it into a weighed quantity of conductivity water. The solution was approximately 0.1 *N* and was stored in a quartz flask.

In all, about 15 g. of the solution was added to the cell in each run. This amount of liquid did not change the height of the solution in the cell sufficiently to change the cell constant appreciably. The resistance at each concentration was measured thrice at 15-minute intervals, each measurement being taken with four known resistances. The average deviation from the average was never more than 0.02%. When the run was completed the cell was removed from the thermostat, the outside was washed and the cell was dried and weighed. The weight of the quartz cell was determined several times during the investigation and found to be constant within 0.01%. This is seen from the following series.

July 14	325.956 g.	August 31	326.003 g.
Sept. 25	326.010 g.	November 30	325.987 g.
May 8	326.015 g.	August 15	325.983 g.

Conductance Data.—The results obtained in this investigation are given in Table II where the values of the equivalent conductance, and the concentration C are shown. The latter is expressed in millimoles per liter. The molecular weights were assumed to be 154.023 for tetramethylammonium bromide, 165.625 for tetra-ethylammonium chloride and 313.212 for tetrapropylammonium iodide. At the head of each sub-table are given

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[8] Schiff and Monsacchi, *Z. physik. Chem.*, **24**, 517 (1897).

the cell constant K, the specific conductance of the water used L_w, and the total weight of the water, W, employed in making up the solution in the cell. These data are shown in Fig. 2 where $1/\Lambda_c$ is plotted against the specific conductance L_s of the solution. In extrapolating to infinite dilution, the *minimum* value for Λ_∞, the conductivity at infinite dilution, is obtained.[9]

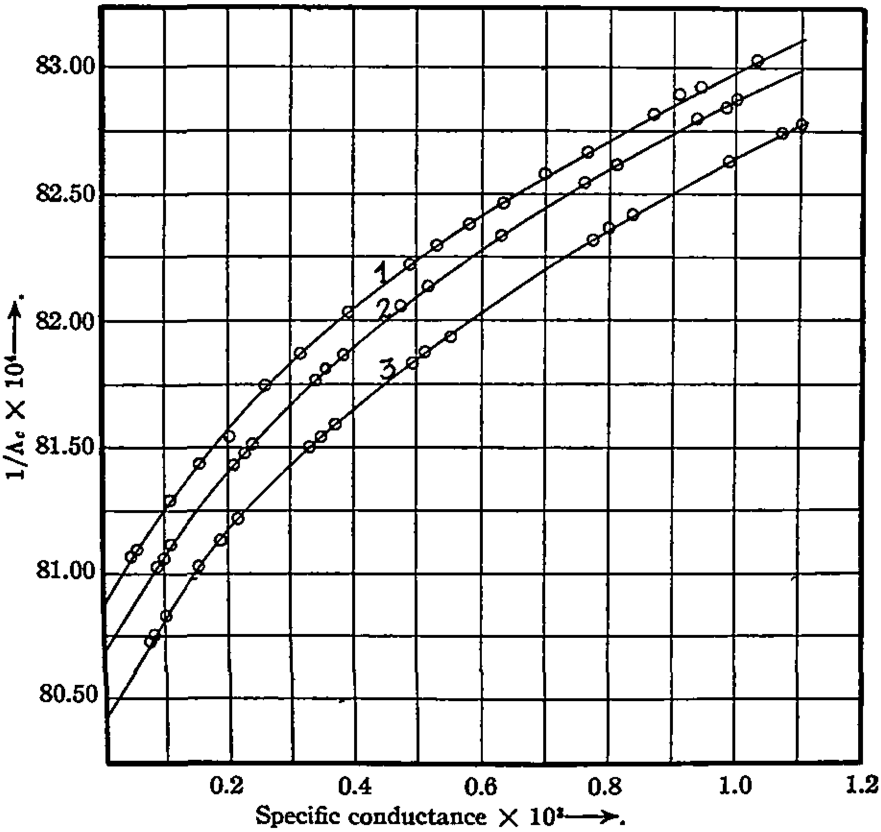

Fig. 2.—1, tetrapropylammonium iodide; add 19.45 to $1/\Lambda_c$. 2, tetraethylammonium chloride; add 10.75 to $1/\Lambda_c$. 3, tetramethylammonium bromide; scale without correction.

Conductance data at round concentrations have been calculated for the three salts. It is possible that these may be published in the International Critical Tables.

Kohlrausch's Rule.—Kohlrausch[10] as early as 1900 had shown that the most accurate conductivity data up to a dilution of 0.001 N were very closely expressed by the simple relation $\Lambda_\infty - \Lambda_c = K\sqrt{C}$. This empirical equation, however, had no theoretical foundation. As a matter of fact, the accepted Arrhenius theory of ionization led to quite a differ-

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[9] Kraus and Parker, This Journal, 44, 2442 (1922). Parker, *ibid.*, 45, 2032 (1923).

[10] Kohlrausch, "Gesammelte Abhandlungen," vol. 2, p. 1137.

ent relationship. The simplicity of the relation and the fact that it reproduced the change of the conductivity with increasing dilution with such exactness led Kohlrausch to insist that it expressed a general law. Washburn,[11] on the other hand, referring to this relationship, contends that "the theoretical basis for the Mass-Action law is so sound that any method which denies the validity of this law as a limiting condition for *all* electrolytes must....be henceforth rejected on this ground alone, if for no other reason." Nevertheless, Kohlrausch's rule has assumed a theoretical significance since the development of the inter-ionic theory of solution based on the assumption of complete ionization.

The equation of Debye and Hückel[12] for a given solute, solvent and temperature contains the square root of the concentration as the only variable. It has been quite definitely established experimentally that the logarithm of the activity coefficient is proportional to the square root of the concentration.[13]

Recently Walden[14] and others applied Kohlrausch's rule to conductivity data. Davies[15] showed that the rule of the square root expresses exactly Weiland's very accurate conductivity data[16] on potassium chloride and Parker's data[17] on hydrochloric acid.

To test this rule on the experimental data obtained in this paper on the alkyl ammonium salts and data in the preceding paper on the alkyl sulfonium salts, the square roots of the concentrations were plotted against the equivalent conductances. It will be seen in Fig. 3, that all these salts give straight lines. If we accept the theoretical significance of the square-root rule ascribed to it by the inter-ionic attraction theory of Debye and Hückel, then these curves indicate that the alkyl-onium salts are completely ionized and are similar to strong electrolytes like potassium chloride and hydrochloric acid.

Whatever the theoretical significance of Kohlrausch's law may be, it is obvious that it expresses exactly the change in conductance with dilution of dilute solutions of strong electrolytes. It leads to the conclusion that in order to obtain the limiting value for Λ_∞ of strong electrolytes, it is not necessary to work with solutions at concentrations below 0.0001 *N*. This is important, inasmuch as the experimental difficulties involved in working with solutions of concentrations below 0.0001 *N* are enormous.

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[11] Washburn, THIS JOURNAL, **40**, 122 (1918).

[12] Debye and Hückel, *Physik. Z.*, **24**, 201, 305 (1923).

[13] For a discussion of the inter-ionic attraction theory and its application, see Noyes, THIS JOURNAL, **46**, 1080, 1098 (1924). Reference to the literature, will be found in this paper.

[14] Walden, *Z. physik. Chem.*, **108**, 341 (1922).

[15] Davies, *J. Phys. Chem.*, **29**, 473, 979 (1925).

[16] Weiland, THIS JOURNAL, **40**, 131 (1918).

[17] Parker, *ibid.*, **45**, 2017 (1923).

The limiting values for Λ_∞ obtained from $\Lambda_c - \sqrt{C}$ curves are considerably higher than those obtained from the $1/\Lambda_c - L_s$ curve. This is shown in Table I, in the second column of which are given the limiting values, Λ'_∞ obtained from a $1/\Lambda_c - L_s$ curve and in the third column are given the values Λ''_∞ obtained from a $\Lambda_c - \sqrt{C}$ curve.

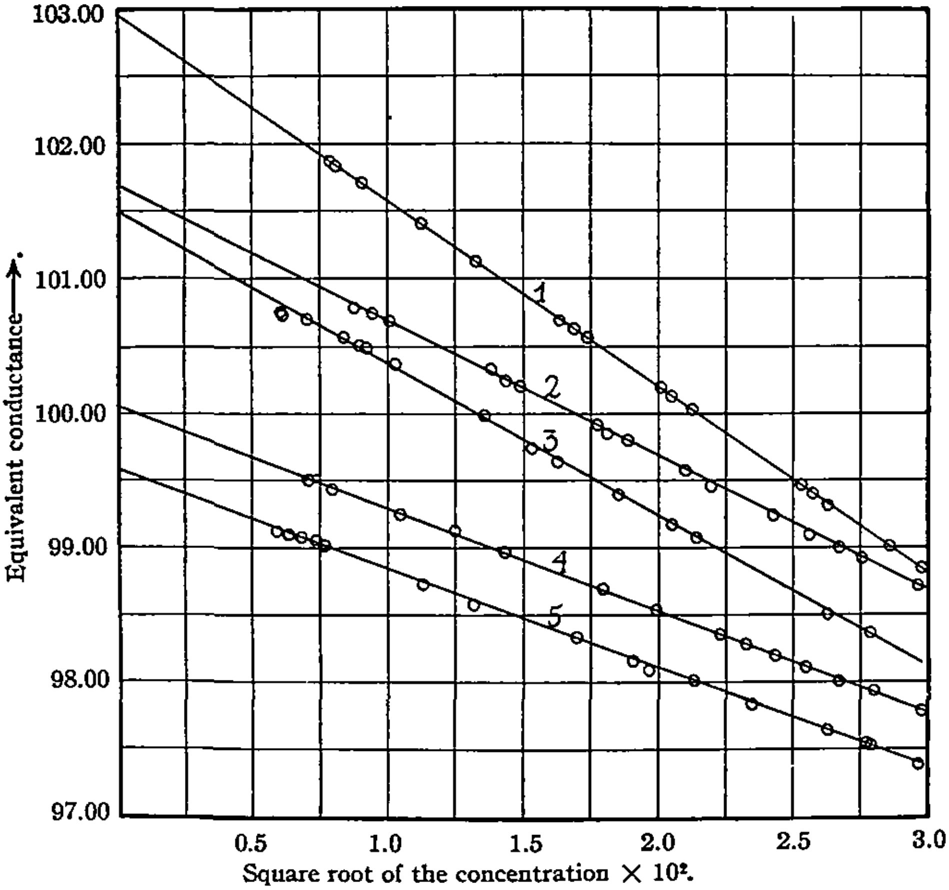

Fig. 3.—1, tetramethylammonium bromide; add 22 to Λ_c. 2, tetra-ethylammonium chloride; add 5 to Λ_c. 3, trimethylsulfonium iodide; add 26.5 to Λ_c. 4, tetrapropylammonium iodide; Λ_c without correction. 5, triethylsulfonium bromide; add 14.2 to Λ_c.

It is difficult to determine which of the two values is the true Λ_∞. It is important to point out, however, that errors inherent in the most accurate

TABLE I

THE MAXIMUM AND MINIMUM VALUES OF ALKYL-ONIUM SALTS

	Λ'_∞	Λ''_∞
Tetramethylammonium bromide	124.34	124.98
Tetra-ethylammonium chloride	109.19	109.73
Tetrapropylammonium iodide	99.69	100.10
Tetramethylsulfonium iodide	127.49	127.76
Tetra-ethylsulfonium bromide	113.49	113.50

experimental work at very high dilution tend to lower this value. Furthermore, the $1/\Lambda_c - L_s$ curves are very much more sensitive to errors in concentration than the $\Lambda_c - \sqrt{C}$ method of extrapolation. These two considerations in addition to the theoretical significance of the square-root rule lead to the conclusion that the maximum value of Λ_∞ obtained by the $\Lambda_c - \sqrt{C}$ curve is probably the more nearly correct value.

Mobilities of the Alkyl Ammonium Ions

Accepting the minimum values for the conductivity of infinite dilutions, obtained from the $1/\Lambda_c - L_s$ curves of Fig. 2, for the time being, we get the following results: tetramethylammonium bromide, 124.34; tetraethylammonium chloride, 109.19; tetrapropylammonium iodide, 99.69. Assuming the mobilities of the chloride, bromide and iodide ion at 25° to be 75.10, 77.44 and 76.12, respectively,[18] we obtain for the limiting values of the tetramethylammonium ion, 46.90 for that of the tetra-ethylammonium ion 34.09, and for that of the tetrapropylammonium ion, 23.57.

TABLE II[a]

CONDUCTANCE OF TETRAMETHYLAMMONIUM BROMIDE

RUN I

$K = 0.0297598$ $L_w = 0.11 \times 10^{-6}$ $W = 1025.37$ g

Concn. × 10^3	Λ_c	Concn. × 10^3	Λ_c
0.062411	123.873	0.404018	122.198
.127691	123.401	.691700	121.331
.268956	122.695	.888060	120.850

RUN II

$K = 0.0308761$ $L_w = 0.12 \times 10^{-6}$ $W = 1005.10$ g.

Concn. × 10^3	Λ_c	Concn. × 10^3	Λ_c
0.065611	123.831	0.453690	122.039
.176888	123.125	.640086	121.478
.302764	122.563	.817980	121.021

RUN III

$K = 0.0227150$ $L_w = 0.15 \times 10^{-6}$ $W = 1021.56$ g.

Concn. × 10^3	Λ_c	Concn. × 10^3	Λ_c
0.002810	123.713	0.420166	122.130
.154064	123.257	.660876	121.402
.285613	122.631	.915818	120.795

Concentration of stock solution = 0.0924498 mole per 1000 g. of solution (weights in air).

CONDUCTANCE OF TETRA-ETHYLAMMONIUM CHLORIDE

RUN I

$K = 0.0305782$ $L_w = 0.17 \times 10^{-6}$ $W = 1023.52$ g.

Concn. × 10^3	Λ_c	Concn. × 10^3	Λ_c
0.102712	108.685	0.591929	107.245
.206856	108.242	.713995	107.006
.330585	107.862	.878990	106.725

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[18] These mobilities have been accepted by Washburn for the "International Critical Tables."

TABLE II (*Concluded*)

RUN II

$K = 0.0331729$ $L_w = 0.14 \times 10^{-6}$ $W = 1009.79$ g.

Concn. × 10^3	Λ_c	Concn. × 10^3	Λ_c
0.08099_1	108.78_0	0.44170_6	107.57_6
$.22253_4$	108.20_1	$.76176_6$	106.93_0
$.35673_8$	107.80_0	$.92240_2$	106.66_9

RUN III

$K = 0.0315693$ $L_w = 0.11 \times 10^{-6}$ $W = 1015.67$ g.

Concn. × 10^3	Λ_c	Concn. × 10^3	Λ_c
0.09021_2	108.74_5	0.48315_6	107.47_5
$.19468_3$	108.33_7	$.65840_0$	107.10_2
$.31509_3$	107.91_6	$.93815_6$	106.63_0

Concentration of stock solution = 0.11518_2 mole per 1000 g. of solution (weights in air).

CONDUCTANCE OF TETRAPROPYLAMMONIUM IODIDE

RUN I

$K = 0.0319859$ $L_w = 0.11 \times 10^{-6}$ $W = 952.11$ g.

Concn. × 10^3	Λ_c	Concn. × 10^3	Λ_c
0.05112_0	99.482_3	0.49952_2	98.352_3
$.11025_0$	99.265_9	$.64771_4$	98.113_2
$.26569_4$	99.821_5	$.89100_0$	97.779_6

RUN II

$K = 0.0321175$ $L_w = 0.095 \times 10^{-6}$ $W = 1008.66$ g.

Concn. × 10^3	Λ_c	Concn. × 10^3	Λ_c
0.060061_4	99.460	0.59292_9	98.199_5
$.15750_0$	99.121_5	$.71555_0$	98.009_8
$.39800_0$	98.539_5	$.93390_0$	97.702_3

Run III

$K = 0.0321080$ $L_w = 0.107 \times 10^{-6}$ $W = 1010.37$ g.

Concn. × 10^3	Λ_c	Concn. × 10^3	Λ_c
0.20695_6	98.973_0	0.78418_8	97.919_5
$.32312_1$	98.698_0	$.96739_8$	97.678_1
$.54247_1$	98.282_0	1.0601_2	97.581_2

Concentration of stock solution = 0.095708_4 mole per 1000 g. of solution (weights in air).

[a] W indicates the total weight of water in a vacuum. The concentrations are expressed in millimoles per liter in a vacuum, and the conductance in reciprocal ohms. The International Atomic Weights of 1924 were used.

The constant of the reference cell was determined with a 0.1 *D* (0.1 mole per 1000 cc. of solution) KCl solution as described by Parker and Parker (Ref. 6a). Its specific conductance at 25° was assumed to be 0.012852_4.

The authors wish to express their thanks to the Directors of the Warren Fund, American Academy of Arts and Sciences, for a grant which has covered part of the expenses of this investigation.

Summary

1. Conductivity measurements with tetramethylammonium bromide, tetra-ethylammonium chloride and tetrapropylammonium iodide between concentrations of 0.06 and 1.0 millimole per liter have been carried out.

A quartz cell and water having a conductivity of the order of 0.1×10^{-6} were used. The solutions were made up by weight with an error of less than 0.05%.

2. Values at round concentrations have been interpolated from the results upon the three salts. These data may be published in the "International Critical Tables."

3. Extrapolation of the results, on the assumption that the mass-action law is approached as a limiting form at infinite dilution, gives a value of Λ_∞ for tetramethylammonium bromide, 124.34, for tetra-ethylammonium chloride, 109.19 and for tetrapropylammonium iodide, 99.69.

4. Assuming that the value of Λ_∞ at 25° of the chloride ion is 75.10, of the bromide ion 77.44 and of the iodide ion 76.12, the values 46.90, 34.09 and 23.57 for the Λ_∞ of the tetramethyl-, tetra-ethyl- and tetrapropylammonium ions, respectively, are obtained.

5. The $\Lambda_c - \sqrt{C}$ curves of the three alkyl ammonium as well as the two alkyl sulfonium salts of the previous paper are straight lines. This corroborates Kohlrausch's rule which assumes a theoretical significance in the theory of complete ionization of Debye and Hückel.

University Heights, New York

[Contribution from the College of Agriculture of the University of Wyoming]

THE NATURAL OCCURRENCE OF ACONITIC ACID AND ITS ISOMERS

By O. A. Beath

Received March 22, 1926 Published August 5, 1926

Review of Literature

Aconitic acid has been reported as being obtained from various plant sources. From the data it is obvious that a compound varying in its melting point from 167° to 191° cannot be in every instance the normal acid, but presumably consists of the normal admixed with its isomeric forms.

Wicke[1] reports the isolation of an acid from *Delphinium consolida* having the same composition as normal aconitic acid. The melting point is not given. His evidence is based upon the composition of the silver salt and the ultimate analysis of the free acid. Parsons[2] detected aconitic acid in sorghum juice by means of characteristic salts. Behr[3] appears to have obtained large quantities of the acid from muscovado sugar and molasses, the composition of which he verified by combustion and formation of the characteristic salts. He proved that lime acting upon the invert

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[1] Wicke, *Ann.*, 90, 98 (1854).

[2] Parsons, *Am. Chem. J.*, 4, 39 (1882).

[3] Behr, *Ber.*, 10, 351 (1877).

sugar did not form the acid, so that it was undoubtedly a naturally occurring substance. Samples of sugar-cane juice from Cuba gave a lead and an acid ammonium salt said to be characteristic of the acid. Through an accident the cleanest portion of the acid was lost, but a small fraction, recovered and purified, gave a melting point of 167°. Behr obtained aconitic acid from West India cane that melted at 172–173°; material from *Aconitum napellus* melted at 165°, from citric acid at 187–188°.

v. Lippman[4] reports aconitic acid in sugar beet products. Yoder[5] found aconitic acid in native sugar cane and gave it a melting point of 183–184°. He states that the low value is probably due to incomplete purification. On the other hand Taylor[6] reports having isolated normal aconitic acid from sugar cane juice and found the substance to melt at 191°. Zerban[7] found aconitic acid in cane juice which melted at 178°. From *Aconitum heterophyllum* Jowett[8] isolated a crop of aconitic acid crystals which melted at 191.5°.

Experimental Part

Six species of native Delphiniums, the *Geyeri, Barbeyi, cuculatum, Nelsonii, bicolor, glaucescens;* two species of *Aconitum*, the *columbianum* (native) and U.S.P. official drug (imported), and one commercial sample labeled aconitic acid from a supply house, have been investigated as to the form of acid by the author.

The plants mentioned gave in each instance an acid melting at 172–173°. The procedure followed was the same for all plants. The air-dried material was macerated with water for a day and after filtering treated with basic acetate of lead. The lead was removed in the usual way (H_2S) and the treatment with lead repeated. When the final solution was quite uniformly free from coloring, it was concentrated slowly and finally agitated with anhydrous ether. The residue from the ether was taken up with purified acetone (hot) the minimum solvent being used, and this quickly diluted with an excess of anhydrous chloroform. On chilling, the acid separated in warty magmas. The acid was further purified by recrystallizing from anhydrous alcohol.

Combustions were made on the free acid and the corresponding ethyl esters. The actual percentages compared very favorably with those calculated in each test. To illustrate, the aconitic acid from *D. Geyeri* gave

	C	H	O
Found, %	41.39	3.57	55.04
Calcd. %	41.38	3.47	55.15

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[4] v. Lippmann, *Ber.*, **12**, 1649 (1879).

[5] Yoder, *J. Ind. Eng. Chem.*, **3**, 640 (1911).

[6] Taylor, *J. Chem. Soc.*, **115**, 886 (1919).

[7] Zerban, *J. Ind. Eng. Chem.*, **11**, 1034 (1919).

[8] Jowett, *J. Chem. Soc.*, **69**, 1521 (1896).

The corresponding ethyl ester gave

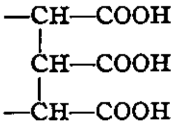
	C	H	O
Found, %	55.63	7.05	37.32
Calcd., %	55.79	7.02	37.19

The conversion of the acid from the ester by acid hydrolysis indicates that the aconitic acid melting at 172–173° is a comparatively stable compound.

The acid from the Aconite sources was not found to vary from that obtained from the native Delphiniums. The commercial sample of aconitic acid was, when purchased, presumed to be the normal acid melting at 191° but upon examination gave a sharp melting point of 173°.

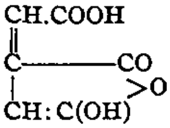
The conductivity value of the commercial sample was approximately the same as that of the acid from the Delphiniums.

Comparative Data.—Rogerson and Thorpe[9] studied the constitution of aconitic acid and concluded that this acid-like glutaconic acid is incapable of existing in forms corresponding to maleic and fumaric acids and that in all probability this property is exhibited by only those derivatives which contain two substituting groups on the methylene carbon atom. Bland and Thorpe[10] prepared labile aconitic acid from the hydroxy-anhydro acid which melted at 173°. The derived acid resembled the normal form in many respects but differed markedly in its behavior on dehydration.

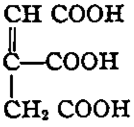


$$\begin{array}{l}\text{—CH—COOH}\\ \quad|\\ \text{CH—COOH}\\ \quad|\\ \text{—CH—COOH}\end{array}$$

Normal acid



Hydroxy-anhydro acid



$$\begin{array}{l}\text{CH COOH}\\ \|\\ \text{C—COOH}\\ |\\ \text{CH}_2\text{ COOH}\end{array}$$

Labile acid

From the structure of aconitic acid two isomeric forms ought to exist, being geometric isomers. Since Bland and Thorpe have established the structure of one isomeric form of aconitic acid melting at 172–173° it seems logical to conclude that the acid occurring in nature having the same characteristics is an identical compound.

The labile aconitic acid prepared by Bland and Thorpe was found by them to resemble the normal acid in most respects but differed markedly upon dehydration with acetyl chloride, being converted into hydroxy-anhydro acid.

Rather and Reid[11] prepared a phenylacyl ester of the normal aconitic acid which melted at 90–91°. Several attempts were made by the writer to obtain a corresponding ester from the isomeric acid isolated from the *Delphinium* and *Aconite* species, but negative results were obtained. This suggests an additional difference between the normal and the isomeric aconitic acids.

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[9] Rogerson and Thorpe, *J. Chem. Soc.*, **89**, 631 (1906).

[10] Bland and Thorpe, *ibid.*, **101**, 1490 (1912).

[11] Rather and Reid, *Arkansas Exptl. Sta. Bull.*, **156** (1918).

Conclusions and Summary

1. The variation in melting points given in the literature for naturally occurring aconitic acid is presumably due to admixtures of two or more definite forms of aconitic acid.
2. Repeated success in the recovery of an acid melting at 172–173° from several species of native plants, and its recovery in the same form from esters point rather clearly to the natural occurrence of an isomeric aconitic acid.

Laramie, Wyoming

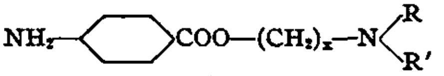
[Contribution from the Chemical Laboratory of the University of Illinois]

THE RELATIONSHIP BETWEEN HYDROGEN-ION CONCENTRATION AND CHEMICAL CONSTITUTION IN CERTAIN LOCAL ANESTHETICS

By Elmer B. Vliet and Roger Adams

Received March 29, 1926 Published August 5, 1926

During the past twenty years a considerable number of local anesthetics of the general type (I), where R and R′ are alkyl or allyl groups and where x is any number greater than one, have been described and several have appeared on the market.



I

In an attempt to correlate the relationship between structure, physical properties and anesthetic efficiencies in these compounds, a large number of anesthetics of this type have been prepared.[1] They will be described in subsequent papers.

From recent work[2] it appears that in any study of the efficiency of local anesthetics, the hydrogen-ion concentrations of their aqueous solutions must be considered. Gros[3] found that the anesthetic efficiency of local anesthetics increases markedly as the hydrogen-ion concentration decreases and recent reports corroborate his findings.

In view of this effect of hydrogen-ion concentration on anesthetic efficiency, the hydrogen-ion concentrations of equimolecular solutions of the anesthetics were determined and are described in this communication. It was hoped that such data might incidentally be of some value as a means

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[1] The authors are indebted to The Abbott Laboratories for kindly furnishing quantities of β-diethylaminoethyl-*p*-aminobenzoate hydrochloride and borate, γ-di-*n*-butylaminopropyl-*p*-aminobenzoate hydrochloride and borate and the borates of β-diethylaminopropyl-*p*-aminobenzoate and β-*n*-butylallylaminoethyl-*p*-aminobenzoate.

[2] Copeland, *Brit. Med. J.*, 1925, II, 547. Regnier, *Bull. sci. pharmacol.*, **31**, 513 (1924); **32**, 513 (1925). Abelin, *Biochem. Z.*, **141**, 458, 470 (1923). Protz, *Arch. exp. Path. Pharmakol.*, **86**, 238 (1920).

[3] Gros, *Arch. exp. Path. Pharmakol.*, **63**, 80 (1910); **67**, 127, 130 (1912).

of ascertaining the relationship between chemical constitution and the basicity of the amines.

Most of the compounds studied were the hydrochlorides of the amino alcohol esters of *p*-aminobenzoic acid. The two principal types of variation in the series were in the R and R′ groups (I) and in the number and arrangement of carbon atoms between the N and O atoms in the alcohol part of the molecule. The compounds before use were all very carefully purified from the proper solvent until successive crystallizations gave no change in melting point. In every instance the compounds were white and well crystallized.

In addition to this main study of the effect of structure on the hydrogen-ion concentrations of solutions of the local anesthetic hydrochlorides, the Sörensen (*P*H) values of a few salts other than the hydrochlorides were also determined.

The determinations of hydrogen-ion concentration were made with the use of the hydrogen electrode in series with a calomel electrode (saturated potassium chloride). The usual procedure was followed and equilibrium was considered to have been reached when there was no appreciable change in e.m.f. after ten minutes. Most of the solutions reached equilibrium quite readily, although some, notably the cyclohexanol derivatives, required nearly an hour.

Rigorous temperature control was not attempted. The room was kept as near to 25° as possible. Due to the high resistance of a few of the solutions, a sharp balance of the potentiometer was somewhat difficult in these cases, although fairly reliable results were obtained by using a rather sensitive galvanometer of the d'Arsonval type. The Sörensen values obtained may be considered as being accurate to about ±0.1 *P*H.

TABLE I

EFFECT OF CHANGES IN THE R AND R′ GROUPS ON THE SÖRENSEN VALUES OF 0.02 *N* SOLUTIONS OF THE HYDROCHLORIDES OF LOCAL ANESTHETICS; BASICITY CONSTANTS

	Nature of grouping between the O and N atoms							
	$=\mathrm{NCH_2CH_2O}$—		$=\mathrm{N(CH_2)_2CH_2O}$—		$=\mathrm{NCH(CH_3)}$- $\mathrm{CH_2O}$—		$=\mathrm{NCHCH_2CHO}$ $\mathrm{CH_2CH_2CH_2}$	
R and R′ groups	*P*H	$K_b \times 10^6$	*P*H	$K_b \times 10^6$	*P*H	$K_b \times 10^6$	*P*H	$K_b \times 10^6$
1. Dimethyl	...	.....	6.2	500	...	...	6.5	2000
2. Diethyl	6.4	1250	6.7	5000	6.3	800	6.7	5000
3. Di-*n*-propyl	6.1	310	6.4	1250	...	...	...	..
4. Di-*iso*propyl	6.3	800	6.9	12000	...	...	...	..
5. Di-*n*-butyl	5.0	2.0	5.6	32	4.9	1.2	...	..
6. Di-*iso*butyl	4.4	0.125	4.5	0.20	...	...	...	..
7. Di-*sec.*-butyl	5.2	5.0	5 4	12.5	...	...	...	..
8. Di-*n*-amyl	4.6	0.32	4.7	0.50	...	...	...	..
9. Di-*iso*-amyl	4.6	0.32	4.5	0.20	...	...	...	..
10. *n*-Butyl allyl	5 3	8.0	5.5	20.0	...	...	...	..
11. *n*-piperidyl	5.9	120	5.9	120.0	...	...	...	..

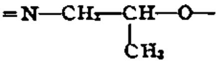
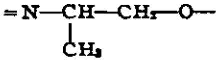
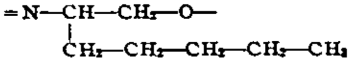
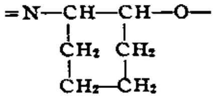
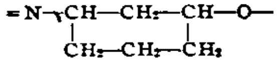
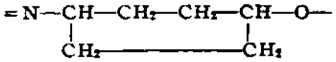
It was found expedient to use solutions of the anesthetics 0.02 *N* with respect to the amount of anesthetic base present. The solutions were prepared as needed by dissolving the compounds in distilled water.

The basicity constants, K_b, for each of the anesthetics were estimated from the Sörensen values by using the approximation developed by Clark,[4] $[H^+]$ approximates $\sqrt{(K_w/K_b)\ [S]}$, where $[S]$ is the concentration of salt. The approximation approaches the facts in cases where the value of K_b is relatively small compared to $[S]$ and where the concentration of positive base ion approximates $[S]$.

The Sörensen values and the basicity constants calculated from them are given in Tables I, II and III.

TABLE II

EFFECT OF CHANGES IN THE NUMBER AND ARRANGEMENT OF THE CARBON ATOMS BETWEEN THE N AND O ATOMS ON THE SÖRENSEN VALUES OF 0.02 *N* SOLUTIONS OF THE HYDROCHLORIDES OF LOCAL ANESTHETICS; BASICITY CONSTANTS

Nature of grouping between O and N atoms	Dimethyl		Diethyl		Di-*n*-butyl	
	PH	$K_b \times 10^6$	PH	$K_b \times 10^6$	PH	$K_b \times 10^6$
1 $=N-CH_2-CH_2-O-$	...	....	6.4	1250	5.0	2.0
2 $=N-CH_2-CH_2-CH_2-O-$	6.2	500	6.7	5000	5 6	32.0
3 $=N-CH_2-CH_2-CH_2-CH_2-O-$	...	....	7.0	20000	...	....
4 $=N-CH_2-CH_2-CH_2-CH_2-CH_2-O-$	...	....	7.1	31000	. .	....
5  $=N-CH_2-\underset{CH_3}{CH}-O-$	...	....	6.2	500	...	....
6  $=N-\underset{CH_3}{CH}-CH_2-O-$	...	....	6.3	800	4.9	1.2
7  $=N-\underset{CH_2-CH_2-CH_2-CH_2-CH_3}{CH}-CH_2-O-$	...	....	4.9	1.2	...	....
8  $=N-\underset{\underset{CH_2-CH_2}{CH_2\quad CH_2}}{CH-CH}-O-$	...	...	(m. p., 216–217°)[a] 6.5	2000	...	....
9  $=N-\underset{CH_2-CH_2-CH_2}{CH-CH_2-CH}-O-$	(m. p., 183–185°) 6.5	2000	(m. p., 179–182°) 6.7	5000	...	....
10  $=N-\underset{CH_2-CH_2}{CH-CH_2-CH_2-CH}-O-$	(m. p., 263–264°)[b] 6.7	5000	...	....	...	....
	(m. p., 220–222°)[b] 6.7	5000	...	...	...	...

[a] This substance is an isomer of the product which melts at 163°, described by Osterberg and Kendall, THIS JOURNAL, **43,** 1370 (1921).

[b] These two products are geometric isomers.

TABLE III

VARIATIONS IN THE SÖRENSEN VALUES OF 0.02 *N* SOLUTIONS OF DIFFERENT SALTS OF LOCAL ANESTHETICS

Substance	Salt		
	Hydrochloride	Acetate	Borate
β-Diethylaminoethyl-*p*-aminobenzoate	6.4	7.1	8.1
γ-Diethylaminopropyl-*p*-aminobenzoate	6.7	...	8.2

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[4] Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., 1922, p. 337.

Discussion of Results

The results of the determinations of hydrogen-ion concentration of the various compounds show a surprisingly consistent relationship to structure. Consequently, the changes in the basicity of compounds of this type may also be directly correlated with the variations in chemical constitution, since the higher the basicity of a substance, the more firmly will the hydrogen ion be held to it.

A few simple relationships are at once apparent. The general tendency is for the basicity to decrease as the size of the R and R′ groups increases (Table I). The dimethylamino compounds, which are slightly less basic than the diethylamino, are exceptions but it is quite common for methyl derivatives to occupy an odd place in such a series. There are also some interesting variations among compounds containing isomeric R groups. Whereas the di-*iso*propylamino compounds are slightly more basic than the di-*n*-propylamino and the di-*iso*- and di-*n*-amylamino products are virtually the same, there is a distinct drop in the basicity of the di-*iso*butylamino compounds from that of their normal and secondary isomers. It is of interest that the basicities of the piperidyl and the *n*-butylallylamino compounds fall between those of the di-*n*-propylamino and di-*n*-butylamino derivatives, as would be expected.

Increasing the number of carbon atoms between the nitrogen and oxygen atoms has an effect just the reverse of increasing the size of the R groups, so long as these carbon atoms are in a straight chain (Table II, 1, 2, 3, 4). However, when carbon atoms are added as side chains, the basicity again decreases. This decrease is only slight when a methyl group is substituted for a hydrogen either on the carbon next to the oxygen or the one next to the nitrogen in the series having only two carbons between the oxygen and nitrogen atoms but is very marked with the *n*-amyl group on the carbon next to the nitrogen (Table II, 5, 6, 7).

The results with the cyclohexanol derivatives indicate that these compounds act as if the nitrogen and oxygen atoms were connected by two straight chains of carbon atoms and that the basicity is determined by the length of the shorter chain. In the diethylamino compound with the oxygen and nitrogen attached to adjacent carbon atoms, thus giving one chain of two carbon atoms and one of six, the hydrogen-ion concentration is practically the same as that of the simple straight-chain compound with two carbons separating the oxygen and nitrogen (Table II, 8; Table I, 2). The hydrogen-ion concentration of the diethylamino compound, having chains of three and five (Table II, 9), is the same as that of the diethylamino derivative with a straight chain of three carbons separating the oxygen and nitrogen (Table I, 2, second column), while the dimethylamino compounds in the same two series differ only slightly. Both geometric dimethylamino isomers, each with two chains of four carbons, are still more basic and the results are in line with the Sörensen values that would be expected of the dimethylamino compound with one straight chain of four carbon atoms between oxygen and nitrogen (Table II, 10).

It is very interesting that these last two geometric isomers (Table II, 10) have Sörensen values that are identical, although their solubilities in water, melting points and anesthetic efficiencies differ greatly.

The Sörensen values of salts formed from weaker acids than hydrochloric agree with those that might be expected. From the stronger bases such as *p*-diethylaminoethyl- and γ-diethylaminopropyl-*p*-aminobenzoate and the weaker acids, salts are formed which are stable in solution but which have Sörensen values higher than those of the hydrochlorides due to the fact that when the salts ionize, the positive ion dissociates into free base and hydrogen ion only to a limited extent, whereas there is a tendency for the negative ion to react with water to form molecules of acid and free hydroxyl ion. However, the acid still furnishes more hydrogen ion than does the positive salt ion, so the compound remains stable.

Attempts were made to dissolve the borates of γ-di-*n*-butylaminopropyl and β-*n*-butylallylaminoethyl-*p*-aminobenzoate in water in order to make determinations of the hydrogen-ion concentration. However, since these compounds are weak bases, their borates were not stable in solution, and quickly hydrolyzed with separation of the free base.

Summary

The hydrogen-ion concentrations of equimolecular solutions of the hydrochlorides of various local anesthetics have been determined.

The effects of changes in structure on the basicity of these compounds have been studied and a few general relations have been pointed out.

The hydrogen-ion concentrations of solutions of a few anesthetic salts formed from weaker acids have been determined and the stabilities of these salts have been discussed.

URBANA, ILLINOIS

[Contribution from the Department of Chemistry, University of Oregon]

PREPARATION AND PROPERTIES OF ORTHO-TOLUIDINE[1]

By H. G. Tanner and Percy A. Lasselle

Received April 14, 1926 Published August 5, 1926

As a dye intermediate *o*-toluidine has its purity specifications. Methods of analyzing this intermediate for its content of *p*-toluidine are numerous. Most of them make use of the colors formed upon the addition of an oxidizing agent such as ferric chloride, potassium dichromate, calcium hypochlorite, and many others. Rosenstiehl[2] pointed out some of these color reactions. He observed, for example, that an aqueous solution of *o*-toluidine hydrochloride formed an insoluble greenish-black precipitate when treated with a cold saturated potassium dichromate solution. Under similar conditions, *p*-toluidine formed a maroon precipitate partly soluble in dilute acid.

Schoen[3] employed these observations as the basis of his method of analyzing *o*-toluidine colorimetrically for the *para* isomer. With mixtures whose *para* content was below 8%, he recommended that a dil. hydrochloric acid solution of the toluidines be treated with potassium dichromate and allowed to stand for an hour during occasional shaking. He stated that "under these circumstances *o*-toluidine gives a black lake, while mixtures of *o*- and *p*-toluidine give a light brown precipitate and a red solution. This is observed in the filtered solution, and the color is more or less intense according to the amount of *p*-toluidine in the mixture."

When Schoen's method was applied to several samples of c. p. *o*-toluidine obtained from different sources, each sample appeared to contain some *p*-toluidine. This was not entirely a surprise, but upon adding definite amounts of *p*-toluidine to these samples the calculated increased percentage of *para* present seldom agreed with the analytical results. The method was put through the usual course of modifications, such as changing the relative concentrations, temperature, etc., with mediocre success. Schoen's statement, "the (red) color is more or less intense according to the amount of *p*-toluidine in the mixture," was found not to be true, unless one interpreted his statement broadly and put undue emphasis upon his expression "more or less."

These results created a strong suspicion that *o*-toluidine itself was partly responsible for the red color which Schoen attributed entirely to the *para* isomer. To prove this there was required some *o*-toluidine prepared

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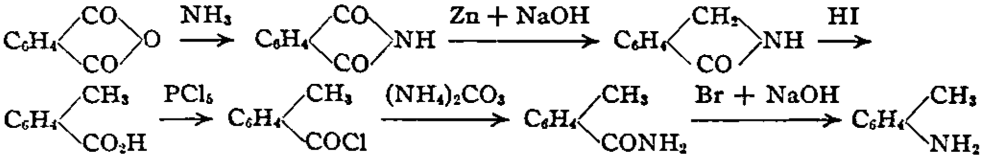
[1] Presented before a joint meeting of the Pacific Coast Sections of the American Chemical Society held in conjunction with the 9th Pacific Division meeting of the American Association for the Advancement of Science, Portland, Ore., June 17-20, 1925.

[2] Rosenstiehl, *Ann. chim. phys.*, [4] **26**, 246 (1872); *Bull. soc. chim.*, **10**, 201 (1868).

[3] Schoen, *Chem.-Ztg.*, **12**, 494 (1888).

in such a manner as to preclude the possibility of any of the *para* compound being present. Phthalic anhydride was selected as the starting material because of its complete freedom from all isomers. From it *o*-toluidine was prepared by the following series of reactions.



Phthalic anhydride was converted into phthalimide by bubbling ammonia through the melted anhydride until absorption ceased.

Phthalide was prepared from phthalimide by the method given by Reissert,[4] and the resultant phthalide converted into *o*-toluic acid by hydriodic acid according to the procedure of Hessert.[5]

o-**Toluyl Chloride from** *o*-**Toluic Acid.**—Fifty g. of *o*-toluic acid was melted in a 250cc. distilling flask and the temperature raised to 120°. A total of 55 g. of phosphorus pentachloride was added and, since the reaction was very vigorous, the chloride was added a little at a time. Upon distillation, the fraction above 205° was collected and converted into *o*-toluamide without further purification. The yields obtained averaged about 75%.

o-**Toluamide from** *o*-**Toluyl Chloride.**—One hundred g. of pulverized ammonium carbonate was placed in a beaker and to it was added, during vigorous stirring, 45 g. of well cooled *o*-toluyl chloride. When the reaction started the mixture became quite warm. For good yields the temperature should be kept low. The reaction was complete in a few minutes and then the ammonium salts were extracted with cold water. *o*-Toluylamide is not appreciably soluble in cold water but dissolves in boiling water from which it may be recrystallized. The recrystallized product melted at 140° instead of 138° as given by Weith;[6] yield, 50%.

o-**Toluidine from** *o*-**Toluamide.**—The transformation of *o*-toluamide into *o*-toluidine by the Hofmann reaction was the most difficult procedure of all. A method was finally evolved which produced a 50% yield.

A solution of 75.3 g. of sodium hydroxide in 189 g. of water was cooled by an ice-bath, and 30 cc. of bromine was added slowly. This solution was kept cool until used. Ninety g. of recrystallized *o*-toluamide was rubbed with water to a thick cream and cooled by an ice-bath. To this was added, in very small portions, the cold sodium hypobromite solution described above. After each addition of the hypobromite the mixture was stirred vigorously for several minutes, the temperature being kept below 5° at all times.

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[4] Reissert, *Ber.*, **46**, 1484 (1913).

[5] Hessert, *Ber.*, **11**, 238 (1878).

[6] Weith, *Ber.*, **6**, 420 (1873).

A solution of sodium hydroxide was prepared from 300 g. of sodium hydroxide and 790 cc. of water. This solution was heated to 75° and to it was added the mixture containing the hypobromite. This addition must be done quickly and in such a manner as to produce as rapid mixing as possible. The resultant mixture was shaken for several minutes and then boiled under a reflux condenser for five minutes. An oily layer of *o*-toluidine appeared on the top of the liquid and was removed by steam distillation.

Purification of the *o*-Toluidine.—The *o*-toluidine was removed from the aqueous distillate by saturating the latter with sodium chloride and extracting with ether. The ether extract was dried overnight with solid potassium hydroxide, filtered, and distilled at 20 mm. pressure. The fraction boiling between 94° and 95° was collected and redistilled at atmospheric pressure (749 mm.) in an atmosphere of carbon dioxide to prevent oxidation. At this pressure, it boiled between 198° and 199°.

The entire amount (32 g.) was dissolved in dil. hydrochloric acid from which solution it was crystallized as the hydrochloride. Several crops of crystals were removed but only the first two were used. These were dissolved in 250 cc. of water and an excess of dil. sodium hydroxide solution was added. The toluidine was extracted with ether and the extract dried with solid potassium hydroxide. After evaporation of the ether, the *o*-toluidine was distilled in an atmosphere of carbon dioxide. Only the middle fraction was saved. It distilled between 200.5° and 200.7° at 754.6 mm. pressure. The thermometer used had a short stem and narrow range. It had been standardized by Thüringisches Staatsprufamt für Glasgerate.

Properties of *o*-Toluidine.—When this *o*-toluidine was treated with potassium dichromate according to the method of Schoen, a green-black precipitate formed. The filtrate from this mixture was bluish-red, practically identical with that given by the *para* isomer. The experiment was conducted at 20°. Repeating it at 5° decreased the amount of precipitate and the intensity of the red color, but by no means eliminated the latter. A solution of 1% *p*-toluidine in pure *o*-toluidine developed a much stronger red color than pure *o*-toluidine alone, which indicates that *p*-toluidine is more easily oxidized.

This proved that Schoen's and probably other colorimetric methods for the determination of *p*-toluidine can yield only approximate results, the error becoming larger with increased purity of sample.

o-Toluidine distilled at 200.6° (754.6 mm.); d_{20}^{20}, 1.0053; n_D^{20}, 1.5688.

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Summary

Schoen's colorimetric method of analyzing *o*-toluidine for its content of the *para* isomer has been shown to be faulty. This was proved by synthesizing *o*-toluidine from phthalic anhydride, thereby avoiding the possibility of any of the *para* isomer being present. However, upon oxidation with potassium dichromate, *o*-toluidine developed a red color indistinguishable from that attributed by Schoen to the *para* isomer only.

The boiling point, density and index of refraction of *para*-free *o*-toluidine were measured.

Eugene, Oregon

[Contribution from the Morley Chemical Laboratory of Western Reserve University]

THE ADDITION OF METHYL HYPOBROMITE AND METHYL HYPOCHLORITE TO CERTAIN ETHYLENE DERIVATIVES

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In a previous paper[1] it was shown that solutions of cinnamic acid and benzalacetophenone in 85% aqueous methyl alcohol at 0° react with bromine with the resulting addition of methyl hypobromite to the unsaturated compounds. In all probability the reaction proceeds as follows: $Br_2 + CH_3OH \rightleftarrows CH_3OBr + HBr$; $>C{=}C< + CH_3OBr \longrightarrow >C(OCH_3)CBr<$. As would be expected the addition of bromine takes place simultaneously. Only one other method of adding methyl hypobromite seems to be on record. By the action of bromotrinitromethane with ethylene derivatives in the presence of the appropriate alcohol, E. Schmidt[2] has added methyl hypobromite and certain other alkyl hypobromites to a number of unsaturated compounds.

The present investigation was undertaken with a view to finding the conditions most suitable for the addition of methyl hypobromite by the reaction of bromine and methyl alcohol with ethylene derivatives and to study the reaction with chlorine. If the reaction proceeds as indicated in the above scheme one would not expect the presence of water to be necessary for the addition of methyl hypobromite. In the preliminary paper, on the basis of tests with solutions of cinnamic acid at 0°, it was stated that in 90% or stronger alcohol the reaction is too slow to be practicable. A more extensive investigation of this point, however, has shown that while the reaction is not feasible with solutions of cinnamic acid in absolute methyl alcohol at 0°, the addition of methyl hypobromite in general takes

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[1] Conant and Jackson, This Journal, 46, 1727 (1924).

[2] Schmidt, Bartholomé and Lübke, *Ber.*, 55, 2099 (1922). Schmidt, Schumacher and Asmus, *Ber.*, 56, 1239 (1923). Schmidt and Bartholomé, *Ber.*, 57, 2039 (1924).

place readily in the absence of water. The reaction in absolute methyl alcohol may be carried out either at room temperature or at the boiling point of methyl alcohol. Although the absorption of bromine in some cases was apparently more rapid at the higher temperature, the advantage of carrying out the reaction in boiling methyl alcohol seems to be principally that of increased solubility. The results obtained with the use of absolute methyl alcohol are summarized in Table I.

TABLE I

REACTION OF ETHYLENE DERIVATIVES WITH BROMINE AND ABSOLUTE METHYL ALCOHOL

Substance	Temp., °C.	Product	Yield, %
Benzalacetophenone	25–30	$C_6H_5CH(OCH_3)CHBrCOC_6H_5$	23
		$C_6H_5CHBrCHBrCOC_6H_5$	5
Cinnamic acid	65	$C_6H_5CH(OCH_3)CHBrCOOCH_3$	34
		$C_6H_5CHBrCHBrCOOCH_3$	30
Stilbene	40–50	$C_6H_5CH(OCH_3)CHBrC_6H_5$	64
		$C_6H_5CHBrCHBrC_6H_5$	19

It was not possible to add methyl hypobromite to maleic acid and β-bromostyrene by this method.

The addition of hypobromous acid by means of the reaction of bromine water with ethylene derivatives is limited[1,3] by the insolubility in water of many unsaturated compounds of high molecular weight. It seemed likely that this difficulty might be overcome, at least partially, by the use of methyl alcohol-water mixtures containing a relatively high proportion of water. Accordingly, the reaction of bromine with a solution of cinnamic acid in 50% aqueous methyl alcohol at 0° was tried. The products were α-bromo-β-hydroxyphenylpropionic acid and α-bromo-β-methoxyphenylpropionic acid in approximately equal amounts; the dibromide of cinnamic acid was also formed in smaller quantity.

The Addition of Methyl Hypochlorite

When solutions of ethylene derivatives in methyl alcohol are treated with chlorine, the addition of methyl hypochlorite to the double linkage of the unsaturated compound takes place. Methyl hypochlorite is doubtless formed by the reaction of chlorine and methyl alcohol in a manner analogous to that described for methyl hypobromite. The reaction was carried out by introducing a stream of chlorine into a vigorously stirred solution of the unsaturated compound in methyl alcohol either at the laboratory temperature or at about 50°. The absorption of chlorine under these conditions was rapid. Table II is a summary of the results.

The mode of addition of methyl hypochlorite to cinnamic acid was shown to be the same as that of methyl hypobromite. By the action of 0.5 *N* sodium hydroxide solution the chloromethoxy ester, which was the prin-

[3] Goldschmidt, Endres and Dirsch, *Ber.*, **58**, 572 (1925).

TABLE II

REACTION OF ETHYLENE DERIVATIVES WITH CHLORINE AND METHYL ALCOHOL

Substance	Temp., °C.	Product[a]	Yield, %
Benzalacetophenone	25–30	$C_6H_5CH(OCH_3)CHClCOC_6H_5$[b]	56
Cinnamic acid	20–30	$C_6H_5CH(OCH_3)CHClCOOCH_3$	55
		$C_6H_5CH(OCH_3)CHClCOOH$	5
Stilbene	40–60	$C_6H_5CH(OCH_3)CHClC_6H_5$[c]	89

[a] No dichloride was isolated in any of the reactions; however, it was probably present in the oil that was formed with each compound.

[b] Assumed to be the β-methoxy compound by analogy with the corresponding bromomethoxy compound.

[c] Stereoisomers.

cipal product of the reaction with cinnamic acid, was hydrolyzed to the corresponding acid. This is the β-methoxy compound, $C_6H_5CH(OCH_3)$-$CHClCOOH$, since it is identical with the chloromethoxy acid formed by adding mercuric acetate[1] to cinnamic acid and replacing the mercury by chlorine.

Goldschmidt[3,4] has recently shown that solutions of ethyl hypochlorite in carbon tetrachloride are sufficiently stable to be used in reactions with compounds containing aliphatic double bonds. The usual reaction under such conditions is the addition of hypochlorous acid; however, in the case of 1,4-dihydronaphthalene, ethyl hypochlorite was added. On account of the solvent value of carbon tetrachloride, it seemed desirable to try the reaction of chlorine on solutions of an unsaturated compound in carbon tetrachloride-methyl alcohol mixtures. Chlorine was found to react rapidly with cinnamic acid dissolved in carbon tetrachloride and methyl alcohol mixtures containing either 50 or 75% of carbon tetrachloride. α-Chloro-β-methoxy-phenylpropionic acid was obtained in both cases by hydrolysis of the reaction products.

Attempts to add methyl hypo-iodite, by treating solutions of cinnamic acid and anethole in methyl alcohol with iodine, were unsuccessful, no apparent reaction taking place.

The application of this reaction to typical primary, secondary and tertiary alcohols along the lines described in this paper is being investigated. The reaction with certain acetylene derivatives is also under investigation.

Experimental Part

The absolute methyl alcohol used in the work described below was the C. P. grade which had been refluxed over quicklime and distilled through a Glinsky still-head; b. p., 65–66°.

I. Addition of Methyl Hypobromite

The introduction of bromine into the reaction solutions was accomplished by drawing a stream of dry air over the surface of liquid bromine contained

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[4] Taylor, MacMullin and Gammal, THIS JOURNAL, 47, 395 (1925).

in a small distilling flask, the side arm of which was connected to the reaction flask by means of a delivery tube. The current of air was dried by passage over calcium chloride and was regulated so as to maintain a small excess of bromine in the solution.

Reaction of Benzalacetophenone with Bromine and Absolute Methyl Alcohol at 25–30°.—A solution of 8 g. of benzalacetophenone in 100 cc. of absolute methyl alcohol at 25–30° was treated with 7.5 g. of bromine vapor during two hours. The products were 4.3 g. of crystals melting at 78–92°, 0.6 g. melting at 68–73° and an oil. A fractional crystallization from methyl alcohol yielded 2.8 g. of α-bromo-β-methoxy-β-phenylpropiophenone melting at 75–76°, 0.7 g. of the dibromide of benzalacetophenone and small amounts of intermediate fractions. Mixed-melting-point determinations showed the substance, melting at 75–76°, to be identical with α-bromo-β-methoxy-β-phenylpropiophenone which was prepared by Middleton[5] by the action of mercuric acetate on benzalacetophenone followed by treatment with bromine.

Reaction of Benzalacetophenone with Bromine and Absolute Methyl Alcohol at 65°.—Seven g. of bromine vapor was introduced into a solution of 8 g. of benzalacetophenone in 100 cc. of absolute methyl alcohol which was boiled under a reflux condenser. About 35 minutes was required to complete the reaction. The yield was 6 g. of substance melting at 64–73° and an oil. Several recrystallizations from methyl alcohol gave pure α-bromo-β-methoxy-β-phenylpropiophenone, m. p , 75–76°.

Reaction of Cinnamic Acid with Bromine and Absolute Methyl Alcohol.—The reaction of cinnamic acid with bromine and absolute methyl alcohol at 0–5° was found to be so slow that it was abandoned. The reaction was tried, therefore, at the boiling point of methyl alcohol. Fifteen g. of cinnamic acid was dissolved in 100 cc of absolute methyl alcohol. The solution was boiled under a reflux condenser and bromine vapor was introduced until 18 g. had reacted. The absorption of bromine was slow, several hours being required to complete the reaction. On cooling the solution to room temperature it deposited 9 4 g of crystals; m. p., 114–115°. The substance is insoluble in sodium carbonate solution. It is probably impure methyl ester of cinnamic acid dibromide, the melting point of which is given in the literature as 117°. By concentration of the solution and recrystallization of the resulting solid material from methyl alcohol, there was obtained 9.5 g. of colorless crystals melting at 65–67°, 0.4 g. of impure dibromide and some oil. The substance melting at 65–67° is insoluble in sodium carbonate solution. It was shown to be methyl α-bromo-β-methoxy-phenylpropionate by its hydrolysis to the corresponding acid and by its preparation from methyl cinnamate, methyl alcohol and bromine.

For its hydrolysis 1.0 g. of substance was heated at about 90° with 0.5 *N* sodium hydroxide solution for 30 minutes. The product was 0.6 g. of crystals contaminated with a small amount of oil. After recrystallization from chloroform it melted at 182–183°; mixtures of the substance with known α-bromo-β-methoxy-phenylpropionic acid melted at the same temperature. The ester was also hydrolyzed by the action of 0 5 *N* sodium hydroxide solution at room temperature for about 24 hours. In this case the product must be purified by boiling with sodium carbonate solution for a few minutes to decompose the dibromide of cinnamic acid which is mixed with the bromomethoxy acid.

Reaction with Methyl Cinnamate.—Schrauth[6] has recently shown that the addition of mercuric acetate to cinnamic acid followed by replacement of the mercury by bromine gives the high-melting isomer of α-bromo-β-methoxy-phenylpropionic acid. A

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[5] Middleton, THIS JOURNAL, 45, 2763 (1923).

[6] Schrauth and Geller, *Ber.*, 55, 2783 (1922).

similar reaction with methyl cinnamate yields the low-melting stereoisomer of this acid. Inasmuch as there was this difference in the products of the reaction of the mercury compound with cinnamic acid and its ester, the reaction of bromine and methyl alcohol with methyl cinnamate was tried. By treating a solution of 10 g. of methyl cinnamate in 100 cc. of methyl alcohol at room temperature with 11 g. of bromine, there were obtained 7.1 g. of methyl α-bromo-β-methoxy-phenylpropionate (m. p., 66–67°) and 6.3 g. of the methyl ester of cinnamic acid dibromide (m. p., 115–116°). A mixture of the bromomethoxy ester thus obtained with the product of the reaction with cinnamic acid (m. p., 65–67°) melted at 65.5–66.5°. Upon hydrolysis with hot 0.5 *N* sodium hydroxide solution the bromomethoxy ester gave the high-melting isomer of α-bromo-β-methoxy-phenylpropionic acid; m. p., 182–183°.

Reaction of Cinnamic Acid with Bromine and 50% Aqueous Methyl Alcohol.—A mixture of 300 cc. of absolute methyl alcohol and 300 cc. of water was saturated with cinnamic acid at 0°. This required 2.7 g. of cinnamic acid. Bromine vapor was passed into the solution, which was kept at 0–5°, until the yellow color of unreacted bromine persisted. Approximately 3 g. of bromine reacted. The colorless precipitate was filtered off and dried. It weighed 0.3 g.; m. p., 179–180°. The filtrate was concentrated to a volume of about 300 cc. and after cooling deposited 1.7 g. of crystals which melted at 175–177°. The remainder of the material was recovered from the solution by extraction with ether. It was a light yellow oil which weighed 2.2 g. The oil soon solidified; recrystallization from benzene gave 1.5 g. of somewhat impure α-bromo-β-hydroxy-phenylpropionic acid melting at 117–123°. Further recrystallization from benzene yielded the pure bromohydroxy acid; m. p., 124–124.5°. Its identity with the product obtained by the reaction of bromine water with cinnamic acid, according to the procedure of Read and Andrews,[7] was established by mixed-melting-point determinations. The 2.0 g. of high-melting material obtained as described above was dissolved in saturated sodium carbonate solution and boiled for a few minutes. The separation of an oil resembling bromostyrene indicated the decomposition of the dibromide of cinnamic acid. The oil was extracted with ether, and acidification of the sodium carbonate solution yielded 1.2 g. of substance melting at 180–181°. After recrystallization it melted at 182–183°; mixed-melting-point determinations showed it to be α-bromo-β-methoxyphenylpropionic acid.

Reaction of Stilbene with Bromine and Absolute Methyl Alcohol.—Five g. of stilbene was dissolved in 250 cc. of hot absolute methyl alcohol into which was passed about 4.5 g. of bromine vapor. The temperature was maintained at 40–50° in order to keep the stilbene in solution. A rapid absorption of bromine resulted and the reaction was complete in about two hours. During the reaction a colorless solid which is principally the dibromide of stilbene separated. At the end of the reaction the solution was heated to the boiling point and filtered. The solid thus obtained melted at 220–230° and is doubtless impure dibromostilbene which has a melting point of 237° when pure. After the separation of the remainder of the material from the filtrate and a fractional crystallization from methyl alcohol the yield was 0.9 g. melting at 220–230°, 0.9 g. melting at 155–175°, 4.8 g. melting at 115–116°, 0.4 g. melting at 112–115° and a small amount of oil. The preparation of an analytically pure sample of the low-melting material proved to be difficult. After several recrystallizations from methyl alcohol it melted at 115–116°, but methoxyl determinations by the Zeisel method gave methoxyl values slightly higher than that calculated for α,β-diphenyl-α-bromo-β-methoxy-ethane ($C_6H_5CH(OCH_3)CHBrC_6H_5$). Since the bromine content was found to be somewhat low, the impurity is not the dibromide. By recrystallizing the subtance melting at 115–116° from benzene or chloroform the separation of some higher-melting substance

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[7] Read and Andrews, *J. Chem. Soc.*, **119**, 1774 (1921).

was effected. Material with an unchanging melting point upon recrystallization, however, could not be obtained by this means. The best results were obtained by repeatedly recrystallizing the substance melting at 115–116° from benzene followed by a final recrystallization from methyl alcohol; the melting point was then 115.5–116.5°.

Anal. Calcd. for $C_{16}H_{15}OBr$: C, 61.9; H, 5.2; OCH_3, 10.7; Br, 27.5. Found: C, 61.3; H, 5.8; OCH_3, 11.6, 11.5; Br, 26.3, 26.4.

II. Addition of Methyl Hypochlorite

Reaction of Benzalacetophenone with Chlorine and Absolute Methyl Alcohol.—Fifteen g. of benzalacetophenone was dissolved in 150 cc. of absolute methyl alcohol. The solution was stirred vigorously while chlorine, dried by passing through concd. sulfuric acid, was introduced at the rate of about two bubbles per second. Occasional tests with moist starch-potassium iodide paper showed the rapid absorption of the chlorine. The reaction temperature was that of the room. When approximately 1.8 liters of chlorine had been passed into the solution its absorption ceased. After distillation of part of the solvent, 11 g. of colorless needles melting at 68–69° was separated. One recrystallization from methyl alcohol gave the pure chloromethoxy derivative of benzalacetophenone; m. p., 69–70°. The remainder of the material consisted of a small amount of the impure chloromethoxy compound and a non-crystalline oil.

Anal. Calcd. for $C_{16}H_{15}O_2Cl$: OCH_3, 11.29; Cl, 12.90. Found: OCH_3, 10.94; Cl, 13.18.

The usual product of the reaction was the chloromethoxy compound melting at 69–70°. In one experiment, however, there was obtained in addition to the compound melting at 69–70° a small amount of material which melted at 98–99° after several recrystallizations from methyl alcohol or toluene. This is probably the other racemate of the chloromethoxy derivative of benzalacetophenone.

Anal. Calcd. for $C_{16}H_{15}O_2Cl$: OCH_3, 11.29. Found: 10.28, 10.09.

The structure of the chloromethoxy compound was not established. However, since the addition of methyl hypobromite to benzalacetophenone yields α-bromo-β-methoxy-β-phenylpropiophenone the substance is probably the β-methoxy compound, $C_6H_5CH(OCH_3)CHClCOC_6H_5$.

Reaction with Cinnamic Acid.—A thoroughly stirred solution of 20 g. of cinnamic acid in 250 cc. of methyl alcohol (b. p., 64–65°) was treated with chlorine in the manner described for benzalacetophenone. The reaction was started at 20° but the temperature soon rose to 30°; the solution was then cooled so that the temperature was maintained at 20–30°. The chlorine was rapidly absorbed and the reaction was complete at the end of one and one-half hours. Distillation of the methyl alcohol yielded a colorless oil. This was dissolved in ether and thoroughly extracted with sodium carbonate solution. From the ethereal solution which contained the material insoluble in sodium carbonate there was obtained 28 g. of oil which soon crystallized; m. p., 46–50°. By recrystallization from methyl alcohol 17 g. of colorless crystals melting at 50–54° was obtained. The residue from the crystallization was an oil containing some crystals. Another crystallization from methyl alcohol of the substance melting at 50–54° gave the pure methyl ester of α-chloro-β-methoxy-phenylpropionic acid; m. p., 54–55°.

Anal. Calcd. for $C_{11}H_{13}O_3Cl$: Cl, 15.51. Found: 15.70.

Mixed-melting-point determinations showed the substance to be identical with the product obtained in the reaction of chlorine and methyl alcohol with methyl cinnamate. Hydrolysis with dil. sodium hydroxide solution gave α-chloro-β-methoxy-phenylpropionic acid.

The acid material resulting from the reaction of cinnamic acid with chlorine and methyl alcohol was recovered by acidification of the sodium carbonate solution obtained in the extraction described above. It was an oil weighing 1.4 g. The oil soon crystallized; m. p., 120–140°. After three recrystallizations from chloroform, colorless crystals melting at 163–164° resulted. A mixture of this substance with about an equal amount of cinnamic acid dichloride (m. p., 163–164°) melted at 148–154°. A mixed-melting-point determination showed the substance to be identical with the product of hydrolysis of the compound melting at 54–55°. It is, therefore, the chloromethoxy derivative of cinnamic acid.

Hydrolysis of the Methyl Ester.—Five g. of the compound melting at 54–55° was hydrolyzed by the action of 0.5 *N* sodium hydroxide solution at room temperature for ten hours. The product weighed 3.1 g. and melted at 135–147°. By recrystallization from methyl alcohol or chloroform the pure chloromethoxy derivative of cinnamic acid was obtained; m. p., 163–164°.

Anal. Calcd. for $C_{10}H_{11}O_3Cl$: C, 55.94; H, 5.16; Cl, 16.52. Found: C, 55.50; H, 5.47; Cl, 16.73.

The chloromethoxy acid undergoes no apparent change when boiled with 0.5 *N* sodium hydroxide solution for about ten minutes. Since this treatment decomposes cinnamic acid dichloride to give chlorostyrene, heating with dilute alkali may be used to purify the chloromethoxy acid which is mixed with the dichloride.

Structure of the Chloromethoxy Acid.—That the compound is α-chloro-β-methoxy-phenylpropionic acid was established by showing its identity with the product of the reaction of chlorine with α-acetoxymercuri-β-methoxy-phenylpropionic acid. The mercury compound was prepared by the reaction of mercuric acetate with cinnamic acid in methyl alcohol solution according to the procedure described in a previous paper.[1] A suspension of 2.2 g. of the mercury compound in 15 cc. of methyl alcohol was treated with chlorine as long as absorption took place. After introducing a small excess of chlorine, it was allowed to stand at room temperature until the presence of free chlorine could no longer be detected by means of moist starch-potassium iodide paper. This process was repeated until all of the solid material had dissolved. The methyl alcohol was distilled, the residue dissolved in ether and the solution thoroughly extracted with concd. aqueous potassium chloride and finally with water. Distillation of the ether gave 1.0 g. of colorless crystals melting at 150–154°. After two recrystallizations from chloroform the substance melted at 163–164°. A mixed-melting-point determination showed the compound to be identical with the product of hydrolysis of the methyl ester obtained in the reaction of chlorine and methyl alcohol with cinnamic acid as described above.

Reaction with Methyl Cinnamate.—By the reaction of chlorine with a solution of 10 g. of methyl cinnamate in 125 cc. of methyl alcohol at 25–30° there was obtained 8 g. of solid melting at 50–55° and an oil. After recrystallization from methyl alcohol the substance melted at 54–55°. A mixture of the compound with the product from the reaction of chlorine and methyl alcohol with cinnamic acid melted at the same temperature. Hydrolysis with 0.5 *N* sodium hydroxide solution gave α-chloro-β-methoxy-phenylpropionic acid; m. p., 163–164°.

Reaction with Cinnamic Acid in Carbon Tetrachloride-Methyl Alcohol Mixtures.—Fifteen g. of cinnamic acid was dissolved in 75 cc. of carbon tetrachloride and to this solution was added 75 cc. of methyl alcohol (b. p., 64–65°). Chlorine was passed into the vigorously stirred solution in the usual manner, a rapid absorption resulting. When about 3 liters of chlorine had been introduced, tests showed the presence of free chlorine. The product was an oil, insoluble in dil. aqueous sodium hydroxide, being probably a mixture of acid esters. Since the oil did not crystallize readily, it was boiled with 0.5 *N* sodium hydroxide solution for about 30 minutes. The small amount of insoluble oil, which is probably chlorostyrene, was extracted with ether. From the aqueous solution was obtained 11 g. of colorless oil which soon crystallized; m. p., 80–140°. Recrystallization from chloroform gave 4 g. of the slightly impure chloromethoxy derivative of cinnamic acid melting at 157–160° and 2 g. of substance melting at 115–130°. The residue from the crystallization was a mass of crystals containing some oil. It undoubtedly contained a considerable amount of the chloromethoxy acid. The material melting at 157–160° after recrystallization melted at 163–164°. A mixture of the substance with known α-chloro-β-methoxy-phenylpropionic acid melted at the same temperature.

The reaction was carried out also in mixtures which contained 75% of carbon tetrachloride and 25% of methyl alcohol by volume. In this case α-chloro-β-methoxy-phenylpropionic acid was obtained by hydrolysis of the reaction product. Its purification, however, was more difficult than when the reaction was carried out in 50% mixtures. A solution of 15 g. of cinnamic acid in a mixture of 120 cc. of carbon tetrachloride and 40 cc. of methyl alcohol was treated with chlorine and the product hydrolyzed as described above. This gave 9 g. of crystals melting at 70–125° and an oil. From the substance melting at 70–125° was obtained by recrystallization 1.5 g. of pure α-chloro-β-methoxy-phenylpropionic acid. The greater portion of the remaining material was a solid melting at 80–105° and was obviously impure. Although the fractional crystallization was not completed, this low-melting material doubtless contained a considerable amount of the chloromethoxy derivative of cinnamic acid.

Reaction of Stilbene with Chlorine and Methyl Alcohol.—Six g. of stilbene was dissolved in 225 cc. of methyl alcohol (b. p., 64–65°). The thoroughly stirred solution was treated at 40–60° with chlorine in the usual manner. A rapid reaction resulted. When the solution had ceased to absorb chlorine the methyl alcohol was distilled until the volume was about 50 cc. Colorless crystals soon separated. These weighed 4 g.; m. p., 80–89°. By concentrating the filtrate 3.3 g. of substance melting at 54–57° and 0.3 g. melting at 42–48° were obtained. The remainder of the material was an oil containing some crystals. After several recrystallizations from methyl alcohol of the substance melting at 80–89° the chloromethoxy derivative of stilbene with a melting point of 96–97° was obtained.

Anal. Calcd. for $C_{15}H_{15}OCl$: OCH_3, 12.57; Cl, 14.38. Found: OCH_3, 12.10, 11.88; Cl, 14.72.

It has not been found possible so far to purify completely the low-melting substance. By recrystallization from methyl alcohol of the substance melting at 54–57° some of the high-melting chloromethoxy compound was separated. After repeating the recrystallization several times, material with a melting point of 55–57° was obtained. A methoxyl determination showed that this substance consisted for the most part of a methoxyl compound. Since the chlorine analyses were high and the methoxyl value was low it seems likely that the material was a mixture of a chloromethoxy derivative of stilbene and the dichloride of stilbene. The chloromethoxy compound is probably a stereoisomer of the compound which melts at 96–97°.

Anal. Calcd. for 85% $C_{15}H_{15}OCl$ + 15% $C_{14}H_{12}Cl_2$: OCH_3, 10.7; Cl, 16.5. Found: OCH_3, 10.4; Cl, 16.4, 16.2.

III. Attempted Addition of Methyl Hypo-iodite

Solutions of iodine in methyl alcohol gave no apparent reaction with cinnamic acid and anethole. Thus, after a solution of 10 g. of cinnamic acid and 1 g. of iodine in 100 cc. of methyl alcohol had stood for 12 months, the color due to the iodine still remained. Likewise, a solution of 1 g. of iodine in 75 cc. of methyl alcohol was not decolorized by 5 g. of anethole after standing for the same period of time.

Summary

1. The presence of water is unnecessary for the addition of methyl hypobromite by the reaction of bromine and methyl alcohol with ethylene derivatives. By the reaction of bromine and absolute methyl alcohol either at 25° or 65° methyl hypobromite was added to benzalacetophenone, cinnamic acid and stilbene. With cinnamic acid, esterification also takes place.

2. A solution of cinnamic acid in 50% aqueous methyl alcohol at 0° reacts with bromine with the simultaneous addition of hypobromous acid, methyl hypobromite and bromine.

3. The action of chlorine on solutions of benzalacetophenone, cinnamic acid and stilbene in methyl alcohol either at 25° or 50° results in the addition of methyl hypochlorite to the double linkage of the unsaturated compound. The product with cinnamic acid was the methyl ester of α-chloro-β-methoxy-phenylpropionic acid. The reaction with cinnamic acid was also carried out with solutions in carbon tetrachloride-methyl alcohol mixtures containing either 50 or 75% of carbon tetrachloride.

4. Attempts to add methyl hypo-iodite to cinnamic acid and anethole with the use of iodine and methyl alcohol were unsuccessful.

CLEVELAND, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE RICE INSTITUTE]

SUBSTITUTED AMIDES. I. THE PREPARATION OF SUBSTITUTED ACETAMIDES AND THE CORRESPONDING PRIMARY AMINES[1]

BY H. O. NICHOLAS AND J. L. E. ERICKSON

RECEIVED MAY 14, 1926 PUBLISHED AUGUST 5, 1926

In 1879 Rudolph[2] showed that a reaction takes place between acetamide and benzyl chloride with the formation of benzylacetamide. On repeating his work for the purpose of ascertaining the general applicability of this reaction in organic synthesis, we noted that the yield of benzylacetamide was very small. Also, a large amount of ammonium chloride was formed in the reaction, a fact which he did not mention. After carefully purifying and drying the alkyl halide and the acetamide, it was found that during the course of the reaction ammonium halide was still formed, and that no halogen acid was evolved. The source of the ammonium halide was determined by passing dry hydrogen bromide through anhydrous acetamide

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[1] Constructed from a thesis submitted by J. L. E. Erickson in partial fulfilment of the requirements for the degree of Master of Science at the Rice Institute.

[2] Rudolph, *Ber.*, 12, 1297 (1879).

at 200–220°, during which process ammonium bromide was abundantly precipitated and diacetamide was formed.[3] The experimental evidence seems to show that alkyl halides react with acetamide in the following manner.

$$CH_3CONH_2 + RBr \longrightarrow CH_3CONHR + HBr$$
$$2CH_3CONH_2 + HBr \longrightarrow CH_3CONHCOCH_3 + NH_4Br$$

Substituted acetamides have been prepared by Titherley[4] by the action of alkyl halides and potassium alkyl sulfates on sodium acetamide. The yields of substituted acetamides obtained by this method were poor. Others[5] have shown that imino ethers, derived from the iminohydrin form of acetamide, when heated in the presence of alkyl halides are converted into the isomeric alkylacetamides.

Experimental Part

Benzyl- and β-Phenylethylacetamides.—A mixture of 0.4 mole of the bromide and 1.6 moles of anhydrous acetamide was placed in a Pyrex flask fitted to a condenser with a ground-glass joint, and heated on an oil-bath for three to six hours at 200–220°. A large amount of ammonium bromide precipitated. The mixture was poured into a concentrated solution of sodium carbonate and the amide was extracted with ether, dried over sodium sulfate and distilled.

Ethyl-, *n*-Propyl-, *n*-Butyl- and *iso*-Amylacetamides.—A mixture of 0.4 mole of the alkyl bromide and 1.6 moles of anhydrous acetamide was placed in a sealed Pyrex tube (65 cm. × 2.7 cm. inside diameter) and heated at 220° until the two layers had disappeared, usually for about 20–30 hours. The method of isolation and purification was the same as described above. β-Phenylethylacetamide was also prepared by this method with the same yield as obtained in the above method.

Table I

Compounds, Properties and Analytical Data

Substituted acetamide	B. p., °C.	M. p., °C.	Yield, %	Analysis Calcd. for	N, %	Found, %
Benzyl-	157 (2 mm.)	61	80[a]	$C_9H_{11}ON$	9.39	9.32
β-Phenylethyl-	154 (2 mm.)	45	40	$C_{10}H_{13}ON$	8.59	8.48
Ethyl-	206	..	66	C_4H_9ON	16.09	15.96
n-Propyl-	225	..	70	$C_5H_{11}ON$	13.86	13.94
n-Butyl-	229	..	66	$C_6H_{13}ON$	12.17	12.25
iso-Amyl-	232	..	42	$C_7H_{15}ON$	10.85	10.94

[a] Benzyl chloride under the same conditions gave but a 51% yield.

On hydrolysis with concd. hydrochloric acid, the corresponding primary amines were obtained in 80–90% yields.

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[3] Strecker, *Ann.*, **103**, 321 (1857). Hofmann, *Ber.*, **14**, 2732 (1881).

[4] Titherley, *J. Chem. Soc.*, **65**, 521 (1894); **79**, 391 (1901).

[5] Wheeler and Johnson, *Am. Chem. J.*, **21**, 185 (1899); *Ber.*, **35**, 164 (1902).

Summary

1. The reaction between acetamide and alkyl bromides, showing its general applicability to the synthesis of substituted acetamides and the corresponding amines, has been investigated.

2. A possible mechanism for the reaction, accounting for the production of ammonium bromide, has been suggested.

HOUSTON, TEXAS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF SASKATCHEWAN]

STUDIES IN URETHANS

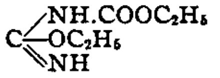
I. MONO- AND DICARBETHOXY-GUANIDINES: DICARBETHOXY-ETHYL-ISO-UREA

BY S. BASTERFIELD AND L. EVELYN PAYNTER

RECEIVED MAY 20, 1926 PUBLISHED AUGUST 5, 1926

During a study of the pharmacological properties of some iso-urea derivatives, it was found by one of us[1] that carbethoxy-ethyl-iso-urea had well-marked physiological action, the chief effects being a mild central depression, a rapid and considerable fall of body temperature, and an increased muscle tonus. The muscular hypertonus suggested an action similar to that of guanidine which is known to stimulate the myo-neural receptors.[2]

It was decided for the purpose of a comparative study to prepare the mono- and dicarbethoxy-guanidines (guanidine mono- and di-formic esters) and examine their pharmacological properties. At the same time it was thought desirable to prepare the dicarbethoxy-ethyl-iso-urea, to determine the effect of introducing a second carbethoxy group into the iso-urea molecule. The compounds may be regarded as urethans, and the study of them is therefore included in a series of studies being carried on in this Laboratory on the chemistry and pharmacology of some mono- and diurethans. Formulas I and II show the structures of the iso-urea derivatives and III and IV the structures of the carbethoxy-guanidines.



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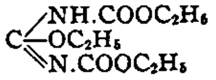

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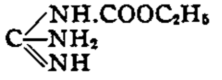

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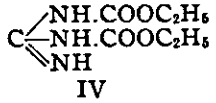

IV

Experimental Part

Dicarbethoxy-guanidine was first prepared by Nencki[3] by the action of ethyl chlorocarbonate on an alcohol solution of guanidine. The mono-

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[1] Basterfield, *J. Pharmacol.*, 20, 451 (1923).

[2] Camis, *J. Physiol.*, 39, 73 (1909).

[3] Nencki, *Ber.*, 7, 1588 (1874).

carbethoxy-guanidine was obtained by the action of alcoholic ammonia upon the di compound, the equation for the reaction as given by Nencki being $2HN{:}C(NHCOOC_2H_5)_2 + 2\,NH_3 = 2\,NH_2.COOC_2H_5 + C_8N_6H_{18}O_4$. It will be noted that a urethan group is split off the dicarbethoxy compound, and also that Nencki uses a double formula for the mono-compound. The production of urethan in this reaction suggested, in part, a study of the decomposition of di-urethans by ammonia and amines, the result of which is reported in another paper.

An alcoholic solution of guanidine (3 molecular proportions) prepared according to Morrel and Bellars[4] was treated with ethylchlorocarbonate (2 molecular proportions) the mixture being cooled and shaken. Fine, white needles were precipitated, which after being recrystallized from alcohol melted at 165° (Nencki gives 162°).

Anal. Calcd. for $C_7H_{13}N_3O_4$· N, 20.68. Found: 20 44.

The yield was 30% calculated on the basis that only one-third of the total guanidine is available for conversion into the ester. Nencki does not state the yield he obtained.

An investigation of the filtrate from the reaction mixture showed that in addition to guanidine hydrochloride, considerable carbonyl-diurethan was present. This must have been formed by hydrolysis of dicarbethoxy-guanidine, and would account for the poor yield of the latter. There is always some water in the alcoholic solution of guanidine, and the hydrogen chloride produced in the reaction would catalyze the hydrolysis. That guanidine itself is not first hydrolyzed to urea is proved by the fact that urea does not react with ethyl chlorocarbonate to give carbonyl-diurethan, but allophanic ester, and neither urea nor allophanic ester was found in the reaction mixture.

Attempts were made to obtain a reaction between ethyl chlorocarbonate and guanidine in the presence of a strong base, contained in a second liquid phase, so that all the guanidine might be available for conversion into the dicarbethoxy compound. The limited solubility of guanidine in solvents other than water and alcohol has so far prevented any successful scheme being devised.

A better method for the preparation of dicarbethoxy-guanidine is by the action of cold alcoholic ammonia on dicarbethoxy-ethyl-iso-urea.[5] A yield of 60% was readily obtained.

Monocarbethoxy-guanidine, $NH_2.C({:}NH).NHCOOC_2H_5$—This was prepared according to the method of Nencki[3] by heating the dicarbethoxy compound with alcoholic ammonia in a pressure bottle at 100° for five hours. The liquid was evaporated and the residue separated by crystallization from alcohol into carbethoxy-guanidine and urethan. The former compound after being dried in the air melted at 99°. After being dried over sulfuric acid in a vacuum it melted at 120°. The melting point changed again to 99° after the crystals had been exposed to the air for a time. The substance of lower melting point is undoubtedly a hydrate. Nencki gives 98° and 114° as the melting points of the two compounds. The yield was 80%.

Anal. Calcd. for $(C_4N_3H_9O_2)_2.H_2O$: N, 29.98. Found: 29.92.

Dicarbethoxy-ethyl-iso-urea, (ethoxy-carbonyl-diurethan), $C_2H_5OOC.N{:}C(OC_2H_5).NHCOOC_2H_5$, was prepared by the method of Dains from the silver salt of carbonyl-diurethan and ethyl iodide. Carbonyl-diurethan was obtained by the action of phosgene on urethan in a benzene-pyridine solution as described by the same investigator.[5]

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[4] Morrel and Bellars, *J. Chem. Soc.*, **91**, 1011 (1907).

[5] Dains, This Journal, **21**, 186 (1899).

The reaction mixture separates into a red oil and a benzene-pyridine layer which contains generally rather more than half of the total product. The red oil may be extracted repeatedly with hot benzene or better simply treated with cold water. The carbonyl-diurethan, which is not very soluble in cold water, is precipitated to a great extent, while pyridine hydrochloride remains in solution. Invariably we found that when the oil was treated with water and the whole cooled in a freezing mixture as suggested by Dains, a mixture of the two compounds separated. Yields as high as 85% were obtained in our later preparations.

In the preparation of the silver salt of carbonyl-diurethan according to the method of Folin[6] it was found that the addition of 1 or 2% of potassium nitrate to the solution of carbonyl-diurethan in alkali accelerated the coagulation of the gelatinous silver compound, so that the precipitate could be rapidly filtered, washed and dried.

The conversion of the silver salt to the ethoxy compound was accomplished most effectively by refluxing a suspension of the salt in dry benzene with ethyl iodide on a water-bath for 28 hours. The solid was removed by filtration and the benzene distilled. The ethoxy compound was obtained as an oil of sweetish odor. It was purified as described by Dains,[5] yield, 83%. The yield was not increased by longer heating, but seemed rather to be diminished. Refluxing in dry ether or standing at room temperature in dry ether for lengthy periods failed to give such good results as were obtained by heating in benzene. The age of the silver salt seemed to be of some importance. Better yields were always obtained with the freshly prepared salt.

Attempts to purify the ethoxy compound by distillation in a vacuum were unsuccessful. At a pressure of 8 mm. most of the oil distilled between 140° and 150°, but no steady boiling point was observed. The distillate was colorless but had a rather unpleasant odor suggesting decomposition. Analysis for nitrogen gave 11.38 and 11.29% as compared with the calculated value 12.07%.

Pharmacological Properties

Preliminary experiments on rabbits were made with the compounds described above.

Monocarbethoxy-guanidine (0.6 g. in aqueous solution) was given by slow intravenous injection to a rabbit weighing 2.8 kg. A mild central depression was produced with a distinct muscular hypertonus. Respiration was rapid and shallow. The rectal temperature fell nearly 3° in one hour. The total effect resembled very closely that of monocarbethoxy-ethyl-iso-urea referred to in the introduction to this paper.

Dicarbethoxy-guanidine was found to be relatively inert though given in doses as large as 0.8 g. to a rabbit weighing only 1.3 kg. There was a fall of temperature of nearly a degree in one and a quarter hours, but this may have little significance in the rabbit.

Dicarbethoxy-ethyl-iso-urea given in doses of 0.35 g. per kilogram by subcutaneous injection was observed to have a powerful physiological action. Drowsiness and incoördination were apparent within five minutes after administration. In 20 minutes, there was deep depression with *complete muscular relaxation*. All reflexes were sluggish. In two hours there were signs of recovery, though after a lapse of five hours, there were still considerable drowsiness and incoördination.

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[6] Folin, *Am. Chem. J.*, 19, 350 (1897).

The rectal temperature fell rapidly during the first two hours, in one animal as much as 4.2° without the production of shivering or rigor.

All animals treated were fully recovered in 24 hours and showed no harmful after-effects.

In comparison with monocarbethoxy-ethyl-iso-urea the dicarbethoxy derivative shows more rapid and intense central depressant action and greater effect on body temperature. There is, however, a complete disappearance of muscular hypertonus with this compound.

Studies in oxygen consumption on animals treated with the iso-urea derivatives indicate that the fall of temperature must be due mainly to increased heat loss. This effect is similar to the antipyresis induced by acetanilide and allied compounds of the aromatic series.

Summary

A study of the methods of preparation of mono- and dicarbethoxyguanidines, and of dicarbethoxy-ethyl-iso-urea, has been made and some modifications of existing methods have been introduced.

Preliminary observations on the pharmacological properties of these compounds are recorded.

SASKATOON, CANADA

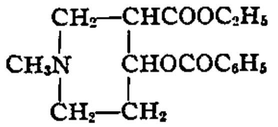
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

PIPERIDINE DERIVATIVES. II. 1-ALKYL-3-CARBETHOXY-4-PIPERIDYL BENZOATES

BY S. M. MCELVAIN

RECEIVED MAY 20, 1926 PUBLISHED AUGUST 5, 1926

In an earlier paper[1] the preparation of a piperidine derivative (I) with essentially the same structure as the piperidine portion of the cocaine molecule was described. It was compared as to physiological action with the compound (II) which has the same characteristic groups but an open-chain structure.



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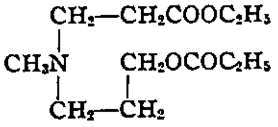

II

Inasmuch as the piperidine derivative possessed considerable physiological activity and the open-chain compound showed practically none, it appeared that a more detailed study of substances of Type I might bring to light some relationship between chemical constitution and physiological action.

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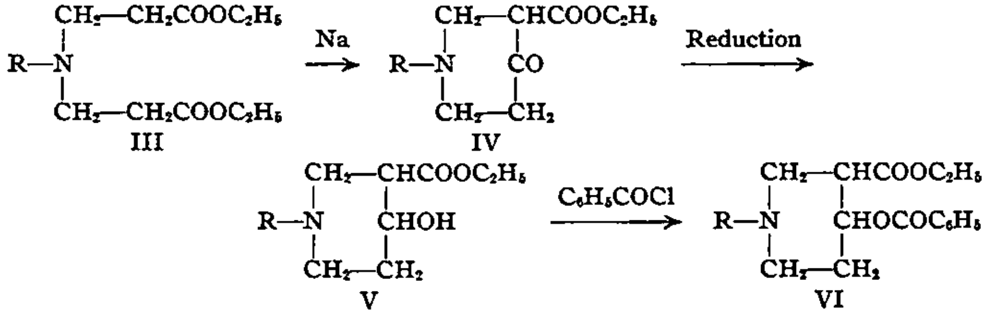
[1] McElvain, THIS JOURNAL, 46, 1721 (1924).

In the procaine series it is well known that the physiological action of the anesthetic is dependent to a considerable extent upon the alkyl groups which are attached to the nitrogen atom. Therefore it seemed that the first point of study of compounds of Type I should be in connection with the various alkyl groups which might be attached to the nitrogen atom.

This paper is concerned with the preparation and brief pharmacological report of a series of these 1-alkyl-3-carbethoxy-4-piperidyl benzoates. The preparation of these compounds is analogous to that of I. The β,β'-dicarbethoxy-diethyl alkyl amines (III) were condensed by sodium to the 1-alkyl-3-carbethoxy-4-piperidones (IV). These piperidones on catalytic reduction yielded the corresponding 4-hydroxy-piperidines (V), which on benzoylation gave the benzoates (VI). These reactions are represented as follows.



The compounds in which R is ethyl, *n*-propyl, *iso*propyl, *n*-butyl, *iso*-butyl, *sec.*-butyl, *n*-amyl and *iso*-amyl have been synthesized. The internal condensations of the diesters took place very smoothly, giving in most cases 50–60% yields of the piperidones. It was noticed that there was a tendency for the piperidone hydrochlorides to remain in a non-crystalline state as the size of the R group was increased. In the case of the *n*-butyl, *iso*butyl and *n*-amyl compounds this tendency lowered somewhat the yields of crystalline material. In the case of the *sec.*-butyl piperidone the hydrochloride could not be caused to crystallize.

None of the hydrochlorides of the 4-hydroxy-piperidines was crystalline. When these substances were purified they were isolated as the free bases by distillation. The butyl and amyl derivatives could not be purified satisfactorily because they decomposed to a very considerable extent on distillation at 1 mm. pressure.

With the benzoates also the tendency to remain in a non-crystalline state was quite marked. Salts of the *iso*propyl, butyl and amyl derivatives crystallized with difficulty and there was always considerable non-crystallizable material in the mother liquors. This difficulty in crystallization was probably due to stereoisomerism, the effect of which was more pronounced as the size of the groups in the 1 position was increased.

Experimental Part

β,β'-Dicarbethoxy-diethyl Alkyl Amines.—A solution of 0.5 mole of the primary alkyl amine in 400 cc. of 95% alcohol was treated with 90 g. (0.5 mole) of ethyl β-bromopropionate. The resulting solution became warm and was vigorously stirred until it cooled. While the stirring was continued, 80 g. of silver oxide was added, followed by 45 g. (0.25 mole) of ethyl β-bromopropionate. The mixture again warmed to some extent and after it had cooled, 40 g. of silver oxide was added. Finally, another 45 g. of ethyl β-bromopropionate and 40 g. of silver oxide were added and the mixture was stirred for two hours. The silver halide was filtered off and washed with 100 cc. of alcohol. The alcohol was removed from the filtrate by distillation and the remaining oil dissolved in 500 cc. of ether. The ether solution was washed twice with a dilute solution of potassium cyanide, after which the ether was removed and the remaining oil distilled under diminished pressure. The tertiary amine fraction was collected over a 10–15° range and was used as such in further syntheses. The yields were from 65 to 75%.

For analyses and physical constants the primary and secondary amines were removed from the tertiary amine by nitrous acid. This treatment gave a constant-boiling product.

TABLE I

β,β'-DICARBETHOXY-DIETHYL ALKYL AMINES

Alkyl group	Formula	B. p., °C. (2 mm)	d^{20}_{20}	n^{20}_D	Analyses, N, % Calcd.	Analyses, N, % Found (Kjeldahl)
Ethyl	$C_{12}H_{23}O_4N$	126–128	1.0058	1.4385	5.71	5.87
n-Propyl	$C_{13}H_{25}O_4N$	132–134	0.9951	1.4393	5.40	5.60
*iso*Propyl	$C_{13}H_{25}O_4N$	128–130	.9960	1.4388	5.40	5.52
n-Butyl	$C_{14}H_{27}O_4N$	154–156	.9804	1.4400	5.12	5.21
*iso*Butyl	$C_{14}H_{27}O_4N$	153–156	.9766	1.4384	5.12	5.18
sec.-Butyl	$C_{14}H_{27}O_4N$	145–148	.9861	1.4415	5.12	5.27
n-Amyl	$C_{15}H_{29}O_4N$	164–168	.9669	1.4375	4.88	5.05
iso-Amyl	$C_{15}H_{29}O_4N$	160–164	.9689	1.4370	4.88	4.95

1-Alkyl-3-carbethoxy-4-piperidone Hydrochlorides.—A solution of 0.15 mole of the β,β'-dicarbethoxy-diethyl alkyl amine in 40 cc. of xylene was added to 3.5 g. of powdered sodium and the mixtureg ently warmed in an oil-bath until the reaction started. The condensation generated sufficient heat to cause the xylene to reflux. After this initial reaction subsided, the mixture was refluxed gently for 20 minutes until all of the sodium had disappeared. The reaction mixture was cooled and treated with 100 cc. of ice water and the resulting suspension extracted with 100 cc. of ether. The aqueous layer was separated, cooled by the addition of ice, and acidified to congo red with hydrochloric acid. Potassium carbonate was then added in excess and the free piperidone base extracted from the aqueous suspension by three 100cc. portions of ether. The ether solution was then treated with dry hydrogen chloride in order to precipitate the hydrochloride. This salt was recrystallized from an alcohol-ether mixture. The yields were 50–60%.

Table II

1-Alkyl-3-carbethoxy 4-piperidone Hydrochlorides

Alkyl group	Formula	M. p., °C.	Analyses, Cl, % Calcd.	Found
Ethyl	$C_{10}H_{18}O_3NCl$	143–145	15.10	15.21
n-Propyl	$C_{11}H_{20}O_3NCl$	138–140	14.23	14.37
*iso*Propyl	$C_{11}H_{20}O_3NCl$	144–146	14.23	14.36
n-Butyl	$C_{12}H_{22}O_3NCl$	127–129	13.48	13.78
*iso*Butyl	$C_{12}H_{22}O_3NCl$	124–126	13.48	13.37
sec.-Butyl	$C_{12}H_{22}O_3NCl$	Noncrystalline	...	...
n-Amyl	$C_{13}H_{24}O_3NCl$	141–143	12.80	12.73
iso-Amyl	$C_{13}H_{24}O_3NCl$	153–155	12.80	13.00

1-Alkyl-3-carbethoxy-4-hydroxy-piperidines.—A solution of 10 g. of the 1-alkyl-3-carbethoxy-4-piperidone hydrochloride in 100 cc. of alcohol was reduced catalytically in the manner which has been described[2] for 1-methyl-3-carbethoxy-4-hydroxy-piperidine. The free base was isolated because the hydrochlorides could not be caused to crystallize. Only the ethyl and two propyl derivatives were isolated, on account of the fact that the higher alkyl derivatives decomposed on distillation. The yields were about 70%.

Table III

1-Alkyl-3-carbethoxy-4-hydroxy-piperidines

Alkyl group	Formula	B. p., °C. (2 mm.)	d^{20}_{20}	n^{20}_D	Analyses, N, % Calcd.	Found
Ethyl	$C_{10}H_{19}O_3N$	130–132	1.0754	1.4712	6.96	7.10
n-Propyl	$C_{11}H_{21}O_3N$	132–133	1.0502	1.4680	6.51	6.58
*iso*Propyl	$C_{11}H_{21}O_3N$	128–130	1.0522	1.4695	6.51	6.63

1-Alkyl-3-carbethoxy-4-piperidyl Benzoate Salts.—The semi-solid amorphous residue obtained after the removal of the solvent from the catalytic reduction of 10 g. of the 1-alkyl-3-carbethoxy-4-piperidone hydrochloride was treated with 20 cc. of benzoyl chloride. This mixture was heated in an oil-bath at 160–170° for 15 minutes. The benzoylation took place rapidly with the evolution of hydrogen chloride. The resulting solution was cooled and diluted with 300 cc. of ether, whereupon an oily precipitate of the hydrochloride of the benzoate formed. This ether suspension was left in an ice box for several hours for crystallization. The ether was then decanted and the hydrochloride recrystallized from an alcohol-ether mixture. The yields of recrystallized material were 40–50% of those theoretically possible from the piperidones.

The *iso*propyl and *sec.*-butyl derivatives could not be crystallized as the hydrochlorides. The free bases were liberated into ether and re-

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[2] Ref. 1, p. 1725.

precipitated as the hydrobromides. These salts finally crystallized after several days of standing in an ice box.

Table IV

1-Alkyl-3-carbethoxy-4-piperidyl Benzoate Salts

Alkyl group	Salt	Formula	M. p., °C.	Analyses, halogen, % Calcd.	Analyses, halogen, % Found
Ethyl	Hydrochloride	$C_{17}H_{24}O_4NCl$	214–216	10.39	10.37
n-Propyl	Hydrochloride	$C_{18}H_{26}O_4NCl$	208–210	10.00	10.15
*iso*Propyl	Hydrobromide	$C_{18}H_{26}O_4NBr$	161–162	20.00	20.05
n-Butyl	Hydrobromide	$C_{19}H_{28}O_4NBr$	194–196	19.32	19.40
n-Butyl	Hydrochloride	$C_{19}H_{28}O_4NCl$	175–177	9.60	9.64
*iso*Butyl	Hydrochloride	$C_{19}H_{28}O_4NCl$	197–199	9.60	9.80
sec.-Butyl	Hydrobromide	$C_{19}H_{28}O_4NBr$	162–164	19.32	19.48
n-Amyl	Hydrochloride	$C_{20}H_{30}O_4NCl$	164–166	9.26	9.24
iso-Amyl	Hydrochloride	$C_{20}H_{30}O_4NCl$	179–181	9.26	9.17

Pharmacological Studies of the 1-Alkyl-3-carbethoxy-4-piperidyl Benzoates[3]

The anesthetic efficiencies of these compounds were determined by applying a 2% solution of the drug to the rabbit's cornea for about one minute and testing the winking reflex every minute to determine the duration of anesthesia. The technique is described in detail by Schmitz and Loevenhart.[4]

Since only small amounts of these drugs were available, their toxicities were determined by subcutaneous injections near the root of the tail in white mice. The minimum lethal dose in Table V is the amount in milligrams per kilogram of body weight which kills at least 50% of the mice injected. The maximum tolerated dose is the largest amount which did not kill more than one out of five mice. The majority of the mice either died or recovered from all symptoms within a few hours and were observed for only 24 hours. Deaths occurring after 24 hours were not attributed to the drugs. The toxic symptoms caused by the drugs were similar to those caused by cocaine. They usually begin in five to ten minutes, the first symptom noted being marked depression. Following this the respiration becomes very rapid and the hind legs become paralyzed. Then the mouse becomes very excited and soon clonic convulsions develop, the mouse throwing itself about the cage or lying on its back or side exhibiting running movements. The convulsions last from ten minutes to two hours and are followed by depression and dyspnea. When the mouse recovered, the respiration gradually became faster and deeper, but in cases terminating in death, the respiration became slower finally ending in irregular gasps. Exophthalmos was observed in the majority of the cases.

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[3] This section is contributed by Ralph E. Jones of the Department of Pharmacology of the University of Wisconsin. The author wishes to express his thanks and to acknowledge his indebtedness to Mr. Jones for this study.

[4] Schmitz and Loevenhart, *J. Pharm. Exptl. Therap.*, **24**, 159 (1924).

TABLE V

PHARMACOLOGICAL RESULTS

Alkyl group	Salt	Duration of anesthesia 2% solution applied to rabbit's cornea for 1 min. Expts.	Av in min.	Toxicity for white mice No. of mice used	Maximum tolerated Mg. per kg.	Minimum lethal Mg. per kg.
Cocaine	HCl	36 31 28 24				
		30 33 29 24				
		32 29	29	18	100	150
Procaine	HCl	No complete anesthesia	..	15	800	900
Methyl	HCl	8 7 10 6				
		9 11 6	8	12	50	100
Ethyl	HCl	No complete anesthesia	..	15	100	150
n-Propyl	HCl	12 12 16				
		22 18 14	16	13	200	250
*iso*Propyl	HBr	13 15 15				
		14 16 18	15	15	120	150
n-Butyl	HCl	36 29 23				
		28 28	29	23	1500	1600
n-Butyl	HBr	27 28 35				
		32 44 35	33	14	1100	1200
*iso*Butyl	HCl	14 13 11				
		15 14 10	13	15	2400	2500
sec.-Butyl	HBr	10 16 17				
		10 17 15	14	13	450	500
n-Amyl	HCl	43 54 47				
		41 43	46	6	3000	4000
iso-Amyl	HCl	44 41 37				
		40 40	40	6	4000	4500

Discussion of Pharmacological Data

It will be noted from these pharmacological studies of Mr. Jones that the toxicity of the *iso*propyl derivative is considerably higher than that of the *n*-propyl derivative and that the *secondary* butyl derivative is likewise much higher in toxicity than the other butyl derivatives. This deviation is explained in part by the fact that the hydrobromide salts were used. As is indicated in the case of the *n*-butyl derivative, these salts show a higher toxicity than the corresponding hydrochlorides.

The striking feature of the series is the marked decrease in toxicity of these compounds as the size of the alkyl group attached to the nitrogen is increased. The increase in anesthetic action with the size of the alkyl group would be predicted, but the toxicity behavior deviates very widely from previous observations on the relationship of structure to physiological action. It is interesting to note that the amyl derivatives show about one-fifth of the toxicity of procaine or one-thirtieth of that of cocaine. At the same time their anesthetic power is considerably greater than that of cocaine.

The solutions of the salts were acid to litmus, and attempts to neutralize them by the addition of sodium hydroxide resulted in precipitation of the free base. This acidity was responsible for the hyperemia and marked irritation which were noted with all of the compounds, and possibly tended to shorten the duration of the anesthesia because of the excessive lacrimation. It is hoped that further modification of the structure will eliminate this objectionable feature.

Summary

Thes yntheses of several 1,3,4-trisubstituted piperidines have been described and some of their properties noted.

The 1-alkyl-3-carbethoxy-4-piperidyl benzoates have very marked local anesthetic action. They show an increase in anesthetic action and a decrease in toxicity as the size of the alkyl radical attached to the nitrogen increases. The amyl derivatives possess a greater anesthetic power than cocaine and show only about one-thirtieth of its toxicity.

As pointed out, the salts of these compounds are acid in aqueous solution and cause irritation and hyperemia.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF AGRICULTURAL CHEMICAL RESEARCH, OKLAHOMA AGRICULTURAL AND MECHANICAL COLLEGE]

A MICRO-COLORIMETRIC METHOD FOR THE ESTIMATION OF PHOSPHOLIPINS IN SEEDS[1]

BY N. B. GUERRANT

RECEIVED MAY 24, 1926 PUBLISHED AUGUST 5, 1926

Introduction

The attention of the biological chemist has been attracted for a number of years to the presence of those phosphorus-containing lipoid substances found in both plant and animal tissues. The universal distribution of these substances seems to indicate that they play an important part in the metabolic processes of the living cell. There is little doubt that they serve as a source of the phosphorus required for building up the complex nucleoproteins of cell nuclei. Indeed it might be said that these substances play an important role in the making of the essential substratum of living matter.

This important class of substances has been designated by Leathes[2] as phospholipins. The exact chemical structure of none of the phospholipins has been definitely established, and the constituents of only a few of them have been approximated.[3] However, a considerable amount of

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[1] Published with the permission of the Director of the Oklahoma Agricultural Experiment Station.

[2] Leathes, "The Fats," Longmans, Green and Co., London, 1910.

[3] Maclean, "Lecithin and Allied Substances," Monograph of Biochemistry, Longmans, Green and Co., 1918.

work has been done upon these substances, most of which has been qualitative in nature rather than quantitative.[4] There is much literature relating the details of the numerous investigations, but we will note only those references pertaining to those investigations which are strictly comparable to ours. We have special reference to a number of articles appearing in the literature concerning the quantitative estimation of the various forms of phosphorus in blood and urine.

While such investigations have helped materially in clearing up the mystery concerning the nature, composition and function of this type of chemical complex, the field of investigation has by no means been exhausted. It is generally conceded that phospholipins occur in varying amounts in all seeds; but we have found no record of an attempt to devise a method for the quantitative estimation of the amount present. Since the phospholipins in seeds appear to play an important part in the metabolism of seeds, and the physiological changes during germination, we have undertaken this investigation in order to devise a quick and comparable method for the estimation of the total phospholipins in various seeds.

Procedure

After much preliminary work in the selection of a suitable solvent, the method of extraction, technique of oxidation, reducing reagent and time allowed for color formation, the following method was adopted.

The material for analysis is first ground until it passes through a 40-mesh sieve. One g. of the dried material is placed in a centrifuge tube and 25 cc. of a 20:80 mixture by volume of ether and alcohol added. The tube is then corked tightly and placed in a shaker where it is shaken vigorously for ten minutes. At the end of this time, the tube is removed from the shaker and centrifuged until all insoluble matter is thrown down. Five cc. of the supernatant liquid is then transferred to a 30–35cc. test-tube which is graduated at 10, 15, 20 and 25 cc. and bent slightly above the last mark. The tube is placed in a hot water-bath until the extract is reduced to a small volume. At this point, a similar tube containing a known amount of a standard phosphate solution is entered in the procedure. One cc. of dil. sulfuric acid (1 part of concd. acid to 2 parts of water) is added to each tube. The tubes are then placed upon a small hot-plate in a somewhat inclined position in such a manner that only the rounded portion of the tube rests upon the hot-plate. The hot-plate should be capable of furnishing sufficient heat to volatilize a portion of the sulfuric acid, but not enough to drive the fumes from the tube. When the contents show the first signs of darkening, small drops of 30% hydrogen peroxide (Superoxol) are carefully added to each tube by means of a small capillary pipet. The hydrogen peroxide is added from time to time as long as any coloration is visible.

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[4] Brauns and MacLaughlin, This Journal, 42, 2238 (1920).

When the last trace of color has disappeared, the heat is gradually increased until the tubes are half filled with sulfuric acid fumes, and they are maintained at this temperature for six minutes. During this period all of the excess of oxidizing agent has been expelled, which is essential to the final development of the true blue color. The tubes are then cooled, the sides rinsed down with water, and the volumes made up to the 10cc. mark. The contents of the tubes are then maintained at a boiling temperature for ten minutes, which is essential to convert all of the phosphate into the ortho form. The tubes are then placed in a water-bath where they are cooled to room temperature. One cc. of a 5% ammonium molybdate solution is added to each tube and the contents are well mixed by shaking. The tubes are removed from the water-bath and 1 cc. of a solution of a 0.4% aminonaphtholsulfonic acid repetition is added. The contents are then mixed thoroughly by shaking and allowed to stand for five to ten minutes depending upon the amount of phosphate present. At the end of this time the tubes are diluted to the mark, and the colors compared. The whole determination can be completed within a period of 60 to 80 minutes.

Reagents

Ether-Alcohol Mixture.—This is made by adding one part by volume of anhydrous ether to four parts of absolute alcohol, and preserving the mixture in a tightly-stoppered container.

Molybdate Solution.—Five g. of C. P. ammonium molybdate is dissolved in 95 cc. of water and the solution preserved in a glass-stoppered container.

Sulfuric Acid.—One part by volume of concd. sulfuric acid is poured into 2 parts of water. (The concentration of this mixture is approximately 12.5 *N*.)

Hydrogen Peroxide.—This is a 30% solution of hydrogen peroxide, which is put on the market by Merck and Company, under the trade name "Superoxol."

Standard Phosphate Solution.—This solution contains sufficient monopotassium phosphate to furnish 0.1 mg. of phosphorus per cc. of solution. The solution is preserved by the addition of a few drops of concd. sulfuric acid before the final dilution.

20% Sodium Sulfite Solution.—This is made by dissolving 20 g. of C. P. sodium sulfite in 80 cc. of water. The solution is unstable and for best results should be made up at 10-day intervals.

20% Sodium Bisulfite Solution.—This is made by dissolving 100 g. of the pure salt in 400 cc. of water. The solution is kept in a tightly stoppered bottle and filtered just before use.

Aminonaphtholsulfonic Acid Reagent.—One g. of purified 1,2,4-*aminonaphthol*-sulfonic acid is added to 225 cc. of 20% sodium bisulfite solution and brought into solution by the addition of small quantities of 20% sodium sulfite solution. The volume is then made up to 250 cc. by the addition of bisulfite solution. This solution is comparatively stable but will darken on standing for a period of several months. For best results, a fresh solution should always be used.

Discussion

The method depends upon the intensity of the color formed as a result of the reduction of the phosphomolybdic acid. The principle was formerly suggested by Taylor and Miller,[5] and later the theory of its action was more fully explained by Wu.[6] Since that time it has been made the basis of a number of determinations pertaining to both blood and urine.[7]

There are some minor details connected with this technique which cannot be stated definitely and this method, as with other methods, must be practiced a number of times before proficiency can be attained. However, in the process of its development several factors have been observed which considerably affect the final results of the determination. Some of these have been reported by investigators working with other materials, while others are noted from our own observations.

One of the first precautions to be observed is in the preparation of the solvent. A number of solvents and combinations of solvents were tried but none proved so satisfactory as a mixture of anhydrous ether and absolute alcohol in the ratio of one part of ether to four parts of alcohol by volume. A mixture of these two solvents had previously been recommended by Schulze.[8] The proportion of the solvents necessary for optimum extraction was obtained by estimating the amount of phosphorus extracted from an equal amount of material by various proportions of the two liquids. The following data give the number of milligrams of phosphorus extracted from 1 g. of material by 25 cc. of a mixture of various percentages of the two components.

TABLE I

RESULT OF EXTRACTING WITH VARIOUS PROPORTIONS OF THE TWO SOLVENTS

Ether by vol., %....	100	90	80	70	60	50	40	30	20	10	0
Alcohol by vol., %..	0	10	20	30	40	50	60	70	80	90	100
Phosphorus, mg.....	11.9	14.6	16.3	19.2	24.1	28.0	33.4	37.6	41.2	31.4	17.9

The exact amount of solvent required to extract 1 g. of material cannot be fixed definitely, as this depends upon the nature and lipin content of that particular seed. With the grain sorghums, it was found that 20 cc. of solvent per gram of material was apparently sufficient to extract all of the lipoid phosphates, but in the determinations reported, this amount was increased by 25% to insure complete extraction. The use of alcohol or ether containing traces of water will result in the extraction of material other than phospholipins. It was found that inorganic phosphates are sufficiently soluble in such a solvent to be responsible for a considerable portion of the color. For this reason, 95% alcohol and ordinary ether can not be used.

The effect of increasing the time of shaking was also noted, but there appeared to be no advantage in shaking longer than ten minutes.

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[5] Taylor and Miller, *J. Biol. Chem.*, **18**, 215 (1914).

[6] Wu, *ibid*, **43**, 189 (1920).

[7] Bell and Doisy, *ibid.*, **44**, 55 (1920).

[8] Schulze, *Z. physiol. Chem.*, **20**, 225 (1895); *Chem.-Ztg.*, **28**, 751 (1914).

Another phase of the determination which offers a fruitful source of errors is the method of oxidation, but with a small amount of material as is required in this determination, it was found to be a simple and reliable operation, when the several factors are reasonably controlled. A deficient amount of sulfuric acid may result in charring and over-heating[9] while the use of an excess of acid will interfere in the final color development.[10] For this reason the amount of acid used must range within rather narrow limits. It is essential that all tubes contain practically the same amount of acid at the end of the digestion, and since the amount of organic material in each test-tube is small, equal volumes of acid are added to each tube before they are placed on the hot-plate. By digesting on such an apparatus an equal amount of heat can be applied to all tubes. One feature of this method of digestion is that the heat is applied to only the bottom of the tube, thus preventing the over heating and subsequent volatilization of the phosphates, which is both possible and probable over a free flame. Another advantage is that several tubes can be digested, at the same time, at practically the same temperature, which is almost impossible with the usual method of digestion. An additional advantage of this method is that bumping is almost entirely eliminated, thus making it unnecessary to use beads or other materials to prevent this usual disturbance. The use of bent test-tubes reduces the chance for loss by bumping to a minimum.

Several oxidizing agents were tried, but hydrogen peroxide proved to be the most efficient and satisfactory. Fuming nitric acid was found to react too violently, while nitric acid and nitrates when not completely expelled by heating, caused a greenish-yellow tint in the solution which interfered with the color comparison. The time required to expel completely all traces of nitric acid is much greater than that required to expel the excess of peroxide.

A number of possible reducing agents were tried, among which were stannous chloride, hydroquinone,[11] β-naphthol, α-naphthol, α-naphthylamine, *p*-aminophenol, and 1,2,4-aminonaphtholsulfonic acid.[12] The hydroquinone and the aminonaphtholsulfonic acid responded most favorably. Of the two, the aminonaphtholsulfonic acid was used, since it reacts in a shorter period of time and produces more color.

Table II gives a comparison of the results obtained by this method with those obtained by the usual gravimetric method, which required a hundred times as much material. These values are the average of three determinations and express the number of milligrams of phosphorus from 1 g. of material.

[9] Baumann, *J. Biol. Chem.*, **59**, 667 (1924).

[10] Whitehorn, *ibid.*, **62**, 133 (1924–25).

[11] MacCallum, *Proc. Roy. Soc.*, **63**, 467 (1898).

[12] Fiske and Subbarow, *J. Biol. Chem.*, **66**, 375 (1925).

TABLE II

MILLIGRAMS OF PHOSPHORUS FROM THE PHOSPHOLIPINS OF 1 G. OF MATERIAL

Subs.	Darso	Red kafir	White kafir	White milo	Feterita
Grav. method	31	42	33	36	26
Micro-col. method	30	40	32	36	27

In conclusion, I take pleasure in thanking Dr. C. T. Dowell, Dr. V. G. Heller, and Mr. W. D. Gallup for their suggestions and coöperation, during this investigation.

Summary

A quick and accurate method for the estimation of the relative amounts of phospholipins in various seeds is described. Results obtained by this method check very satisfactorily with those obtained by the usual gravimetric method, which requires a hundred times the amount of material. The phospholipin content of a number of seeds has been determined. A few results are given here in order to show the accuracy of the method, and other results will be published in due time.

STILLWATER, OKLAHOMA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

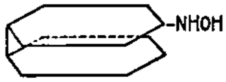
BETA-XENYLHYDROXYLAMINE AND ITS REARRANGEMENT

BY HENRY GILMAN AND JAMES E. KIRBY[1]

RECEIVED MAY 24, 1926 PUBLISHED AUGUST 5, 1926

Introduction

The reactions of a number of diphenyl derivatives have been interpreted on the basis that the two phenyl groups have at times a bi-planar and not a co-planar configuration.[2] If this is the case with β-xenylhydroxylamine, then one of its bi-planar formulas can be represented as follows.



Aryl hydroxylamines undergo ready rearrangement, particularly under the influence of mineral acids, to give aminophenols, the hydroxyl group rearranging to the *para* and, to a less extent, to the *ortho* position. Be-

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[1] This paper is an abstract of a part of a thesis presented by James E. Kirby in partial fulfilment of the requirements for the degree of Master of Science in Chemistry at Iowa State College.

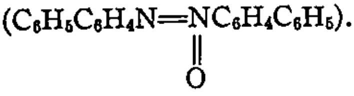
[2] Kaufler, *Ann.*, **351**, 151 (1907); *Ber.*, **40**, 3250 (1907). Cain, Coulthard, and Micklethwait, *J. Chem. Soc.*, **101**, 2298 (1912). Cain and Micklethwait, *ibid.*, **105**, 1437 (1914). Turner, *ibid.*, **107**, 1495 (1915). Kenner and Stubbings, *ibid.*, **119**, 593 (1921). Christie and Kenner, *ibid.*, **121**, 614 (1922). Adams, Bullock and Wilson, THIS JOURNAL, **45**, 521 (1923). Raiford and Clark, *ibid.*, **48**, 485 (1926).

cause of the proximity of the *p*′ or 4′ position in the above bi-planar formula for β-xenylhydroxylamine, there is the possibility that on rearrangement the hydroxyl group might go to the *para* position of the second phenyl group to give the known 4-amino-4′-hydroxydiphenyl ($4\text{-}NH_2C_6H_4.C_6H_4OH\text{-}4'$).

It has been shown that a rearrangement of this type does not take place. This agrees with related work reported recently by Raiford and Clark.[3] They obtained the acetyl-benzoyl derivatives of 4-amino-4′-hydroxydiphenyl in isomeric forms that showed no tendency to rearrange. This behavior opposes the theory that Positions 4 and 4′ in diphenyl derivatives are fixed relatively as suggested by the Kaufler-Cain bi-planar formula.

Rearrangements of the kind shown by arylhydroxylamines can be better studied by other classes of compounds. For example, the allyl ethers of phenols and the bromo- and chloro-anilines undergo smooth rearrangements to the *para* and, to a smaller extent, to the *ortho* positions. Studies now in progress on the allyl ether of *p*-hydroxydiphenyl and on *p*-bromo-aminodiphenyl ($p\text{-}BrNHC_6H_4.C_6H_5$) show that the allyl group and the bromine rearrange almost exclusively to the *ortho* position to the hydroxyl and amino groups, respectively. These are hardly unexpected results inasmuch as it is well known that when the *para* position is blocked (and a phenyl group blocks the *para* position in diphenyl derivatives) the group that rearranges enters the *ortho* position. Obviously a more satisfactory test for the bi-planar formula in rearrangements of this type is to be found in compounds where the two *ortho* positions are blocked. Then, if any rearrangement takes place, and if the *ortho* substituents are of the kind that do not submit to displacement, the group that rearranges should go to the second phenyl group inasmuch as *meta* rearrangement rarely occurs and then only to a very limited extent.

Experimental Part

The β-xenylhydroxylamine was prepared in the customary manner by reducing *p*-nitrodiphenyl by means of zinc dust in a neutral alcoholic solution. The hydroxylamine was precipitated by pouring into water. At first it was virtually impossible to obtain the hydroxylamine by filtration. It is unusually sensitive[4] to oxidation and is readily and almost completely converted to *p,p*′-azoxybisbiphenyl  $(C_6H_5C_6H_4N{=}\underset{\underset{O}{\|}}{N}C_6H_4C_6H_5)$. The dilute alcoholic solution prior to filtration showed the usual reactions for

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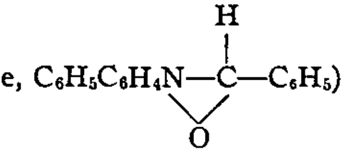
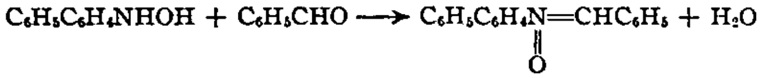
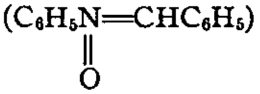
[3] Raiford and Clark, Ref. 2, p. 483.

[4] Diphenylhydroxylamine ($(C_6H_5)_2NOH$) has been prepared from the Grignard reagent by Wieland and Roseeu [*Ber.*, 45, 494 (1912); 48, 1117 (1915)]. It, too, is unusually unstable. 4,4′-Di-β-hydroxylaminodiphenyl ($HONHC_6H_4.C_6H_4NHOH$) has been prepared by Fischer and Hepp [*Ber.*, 20, 2471 (1887)] by a diazo-coupling reaction.

an arylhydroxylamine. In particular, it underwent ready condensation with benzaldehyde to give the corresponding α-phenyl-N-xenylnitrone (or N-α-epoxy-N-xenylbenzylamine,  $C_6H_5C_6H_4\underbrace{N-\overset{\displaystyle H \atop |}{C}}_{O}-C_6H_5$) as follows.



$$C_6H_5C_6H_4NHOH + C_6H_5CHO \longrightarrow C_6H_5C_6H_4\underset{\underset{\displaystyle O}{\|}}{N}=CHC_6H_5 + H_2O$$

This nitrone was prepared also according to the suggestive work of Gattermann[5] who reduced nitrobenzene electrolytically in the presence of benzaldehyde in order to arrest reduction at the hydroxylamine stage by having it combine *in situ* with benzaldehyde to form the corresponding nitrone. The α-phenyl-N-phenylnitrone ( $C_6H_5\underset{\underset{\displaystyle O}{\|}}{N}=CHC_6H_5$) was prepared previously by Bamberger[6] from β-phenylhydroxylamine and benzaldehyde. These nitrones undergo ready hydrolysis by mineral acids to the corresponding hydroxylamine and aldehyde, and the rearrangement reactions of β-hydroxylamines can be carried out by means of them.[5,6]

The β-xenylhydroxylamine was finally prepared in a pure condition by pouring the reduction mixture of *p*-nitrodiphenyl first into some acetic acid and then into water. The dil. acetic acid was found to render the hydroxylamine less sensitive to oxidation. When so prepared it could be filtered and dried and was comparatively quite stable.

Reduction of *p*-Nitrodiphenyl.—In all experiments 5 g. of *p*-nitrodiphenyl was added to 250 cc. of 95% alcohol, 30 cc. water, 3 g. of ammonium chloride and 5 g. of zinc dust. The mixture was cooled by running water until no heat of reaction was evident, and stirring was then continued at room temperature for 30 minutes. On filtering the mixture into an equal volume of water, an almost white precipitate formed at once. When filtered it was found to have undergone, in a very short time, conversion to the *p,p'*-azoxybisbiphenyl, melting[7] at 207.5°. The identity of the azoxy compound was confirmed by analysis and by a mixed-melting-point determination of the same compound prepared according to the method of Zimmermann.[7]

Anal. Calcd. for $C_{24}H_{20}ON_2$: N, 8. Found: 8.32.

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[5] Gattermann, *Ber.*, **29**, 3040 (1896).

[6] Bamberger, *Ber.*, **27**, 1548 (1894), etc. A paper with new observations and corrections from his earlier extensive publications has appeared recently [*Ber.*, **57B**, 2082 (1924)].

[7] The temperatures recorded in this paper are uncorrected. The azoxy compound was crystallized from glacial acetic acid, in which it is sparingly soluble. It melts several degrees higher than the temperature given by Zimmermann, [*Ber.*, **13**, 1960 (1880)].

Preparation of α-Phenyl-N-xenylnitrone.—The nitrone was prepared in three ways: first, benzaldehyde was added to the precipitated hydroxylamine prior to filtration and in the absence of acetic acid; second, the reduction of *p*-nitrodiphenyl was carried out in the presence of benzaldehyde; third, the benzaldehyde was condensed with the hydroxylamine after filtration of the dil. acetic acid solution. It is obtained pure as a yellow compound melting at 174–175° when recrystallized from alcohol.

Anal. Calcd. for $C_{19}H_{15}ON$: C, 83.5; H, 5.5; N, 5.1. Found: C, 83.1; H, 5.5; N, 5.5.

The nitrone is readily hydrolyzed to benzaldehyde by means of dil. hydrochloric and sulfuric acids. When hydrolyzed with dil. mineral acids in a current of steam to remove benzaldehyde, and then treated with slightly stronger mineral acids in order to effect the hydroxylamine rearrangement, no 4-amino-4′-hydroxydiphenyl was obtained. Under these conditions *p*-aminophenol is formed from the corresponding α-phenyl-N-phenylnitrone.[5,6]

Preparation of β-Xenylhydroxylamine.—The reduction mixture of *p*-nitrodiphenyl, alcohol, water, ammonium chloride and zinc dust was filtered into 15 cc. of glacial acetic acid. *This solution, not entirely clear, was filtered into a volume of water equal to* that of the reduction mixture and acetic acid. A pale yellow precipitate of the β-xenylhydroxylamine formed. It melts with preliminary softening and decomposition at 158° and is readily soluble in ether, acetone, alcohol and glacial acetic acid, and somewhat less soluble in benzene.

Anal. Calcd. for $C_{12}H_{11}ON$: N, 7.57. Found: 7.59, 7.84.

Like the hydroxylamine that is precipitated by water containing no acetic acid it gives the characteristic tests of hydroxylamine with Fehling's solution and ammoniacal silver nitrate, and forms the α-phenyl-N-xenylnitrone with benzaldehyde.

The authors wish to acknowledge help from Professor W. H. Perkin and Mr. L. C. Heckert.

Summary

β-Xenylhydroxylamine has been prepared by the reduction of *p*-nitrodiphenyl. It does not rearrange to 4-amino-4′-hydroxydiphenyl.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

OPTICALLY ACTIVE DYES. III. PHYSICAL PROPERTIES, DYEING REACTIONS AND MECHANISM OF DYEING

BY WALLACE R. BRODE[1] WITH ROGER ADAMS

RECEIVED MAY 24, 1926 PUBLISHED AUGUST 5, 1926

In the previous papers[2] of this series a method was described for the preparation of optically active dyes and the physical properties of the basic dyes of this type were studied as to their suitability for use in the experiments on the absorption of dyes by fibers. This paper describes the re-

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[1] This communication is an abstract of a portion of a thesis submitted by Wallace R. Brode in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

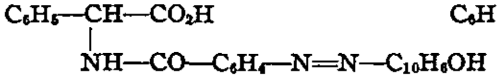
[2] (a) Ingersoll with Adams, THIS JOURNAL, **44**, 2930 (1922). (b) Brode with Adams, *ibid.*, **46**, 2032 (1924).

sults of careful dyeing experiments on wool and silk with the active and racemic modifications of certain dyes in the hope of determining whether chemical action takes place in the dyeing process.

It has been shown by analysis[3] that fibers such as wool and silk contain asymmetric compounds in their active forms and since the rates of reaction of enantiomorphic substances combining with the same active constituent are in general known to be different, it was considered probable that the combination of active dyes with fibers would have a different rate if the action were chemical; or rather it may be stated that if the absorption rates of the active forms of a dye were different or if a selective absorption occurred with a racemic modification, then this effect might be attributed to a chemical action between the dyes and the active part of the fiber. The results showed no difference in rates of the *d*- and *l*-forms and no selectivity with racemic modifications, and consequently no proof that chemical action takes place has been demonstrated.

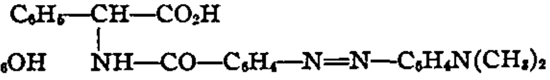
In addition to the work on the selective absorption by fibers to which references were given in the first articles in this series there should be mentioned the work of Euler and Bucht[4] who showed that casein (whose constitution as a protein is similar to that of fibers) shows no selective absorption of α-bromopropionic acid under the most favorable conditions where approximately half the acid in solution was absorbed. Similar data have been obtained upon the absorption of stereoisomeric compounds by active and inactive absorption agents and in no case has any evidence of selective absorption of active isomers been obtained.[5]

In this investigation the β-naphthol (I) and dimethylaniline (II) coupling products of diazotized *d*-, *l*- and *dl*-phenyl (*p*-aminobenzoylamino)acetic acid, the dyes prepared first by Ingersoll and Adams,[2a] were made again, carefully purified and studied. In order to have the results in the dyeing experiments of value, the determination of the exact amount of dye absorbed must be accurate and the dyes must be pure.



$$\begin{array}{l} C_6H_5-CH-CO_2H \\ \qquad\quad | \\ \qquad\quad NH-CO-C_6H_4-N=N-C_{10}H_6OH \end{array}$$

I



$$\begin{array}{l} C_6H_5-CH-CO_2H \\ \qquad\quad | \\ \qquad\quad NH-CO-C_6H_4-N=N-C_6H_4N(CH_3)_2 \end{array}$$

II

The best methods for the determination of the strength of dye solutions have been studied recently.[6] The three methods generally used are those

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[3] Matthews, "Textile Fibres," John Wiley and Sons, New York, 1913. Abderhalden, *Z. physiol. Chem.*, **46**, 31 (1905). Georgievics, "Chemical Technology of Textile Fibres," Scott, Greenwood and Sons, New York, 1920. Bowman, "Structure of Wool Fibres," Macmillian and Co., Ltd. London, 1908.

[4] Euler and Bucht, *Z. anorg. Chem.*, **126**, 267 (1922).

[5] Hermans, *Z. physik. Chem.*, **113**, 385 (1924), Freundlich, "Kapillarchemie," Akademische Verlagsgesellschaft m. b. H., Leipzig, 1923, 268, 1189.

[6] (a) Appel, Brode and Welch, *Ind. Eng. Chem.*, **18**, 627 (1926). (b) Calcott and English, *ibid.*, **15**, 1042 (1923).

of titration by titanous chloride in case the dye is reducible, determination by spectrophotometric measurements and by comparative dyeing tests. Under usual conditions the error in the amount of dye determined by the first two methods is about ±0.5% though in many cases the determination may be more accurate. The dyeing method is accurate to about 2% in the blue and green, and the error is probably much larger in the red and yellow. The titanous chloride method was used in this work for determining the strength of the exhausted solutions and the dye samples were studied photometrically. In no case was one dye absorbed more rapidly than its mirror image, nor was an active solution ever produced by treatment of a racemic dye solution with wool or silk.

The results of the dyeing experiments just mentioned are at variance with those obtained by Porter and Hirst[7] and particularly with those by Porter and Ihrig[8] who presented data that certain azo dyes obtained from *m*-aminomandelic acid showed a selective absorption toward fibers for one of the enantiomorphic forms. The dyes described by Porter and Ihrig were made again and their dyeing experiments were repeated. The results of these authors could not be checked. No selectivity could be found, a fact which confirms the results with the dyes from phenylamino-acetic acid. More details of work on Porter and Ihrig's dyes are described in the following paper.

Since the completion of this investigation there has been published by Morgan and Skinner[9] a paper on stereoisomeric azo dyes. These were prepared by coupling various diazonium salts with diphenyl-β,γ-diamino-*n*-butane. The resolutions into the active forms were then carried out on the racemic dye, thereby presenting an entirely different method for the preparation of optically active dyes from that used by Porter and Ihrig and by Ingersoll and Adams. Morgan and Skinner claim to have observed a slight selectivity for the *l*- form of *dl*-di-4′-sulfobenzene-di-4-azodiphenyl-β,γ-diamino-*n*-butane, as compared with the *d*- form, using the titanous chloride method to determine the strength of the exhausted dye bath. Their conclusions were based on a difference of dye content of 0.0003 g. of dye as detected by titration of 5 cc. of the solution. With very dilute solutions of dyes such as were used, the accuracy cannot possibly be so great as that established for the titration of more concentrated solutions, and consequently a difference so slight as that found can hardly be considered within the experimental error of the analytical method. Moreover, the experimental evidence of these authors is that the observed difference in absorption is only slightly greater than the actual error in titration of the solutions. The amount of *l*-dye by weight per 100 cc. of solution was

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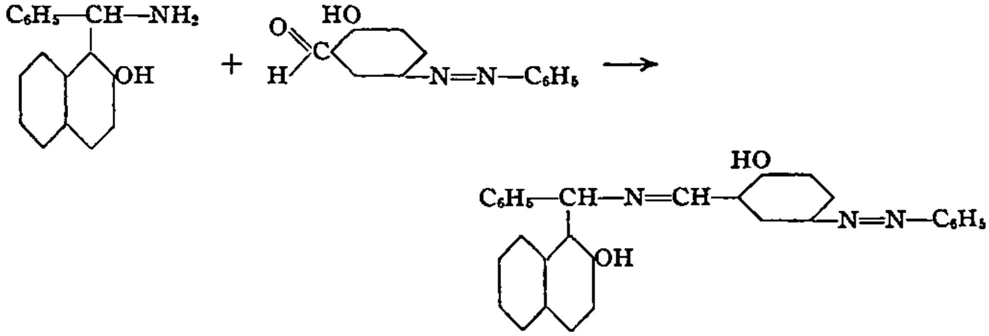
[7] Porter and Hirst, This Journal, **41**, 1264 (1919).

[8] Porter and Ihrig, *ibid.*, **45**, 1990 (1923).

[9] Morgan and Skinner, *J. Chem. Soc.*, **127**, 1731 (1925).

0.4545, and the amount of *d*-dye by weight per 100 cc. was 0.4575 but the titrations on these two solutions were both given as exactly the same. It must also be considered that the *l*-dye varied widely in rotation depending upon the alkaloid used for resolution, and that the rotation of the *d*- and *l*-forms studied differed by more than 5%. With all these facts considered and the numerous possible and probable ways of explaining the experimental results besides that by selective absorption, the conclusion that selective absorption has been demonstrated seems entirely unwarranted.

Another type of dye (III) which it has been hoped could be used for tests similar to those just described was that obtained by the condensation of benzene-azosalicylaldehyde and the various stereoisomeric forms of α(β-naphthol)benzylamine. No difficulty was found in preparing the active and racemic dyes, but unfortunately they were so insoluble as to give unsatisfactory results in dyeing experiments.



III

Experimental Part

Preparation of Dyes.—The method used for preparing the dimethylaniline and β-naphthol coupling products of phenyl(*p*-aminobenzoylamino) acetic acid was essentially that described by Ingersoll and Adams except that the resolution of the *d*-form of phenylamino-acetic acid was carried out according to the more recent directions of Ingersoll.[10] The purification of the dimethylaniline dyes was more satisfactorily accomplished by crystallization from ethyl acetate than from 50% alcohol as was previously done by Ingersoll.[10]

Physical Properties.—The physical properties of the β-naphthol dyes were discussed in detail in a previous paper.[2a] The determinations of the physical properties of the dimethylaniline dyes were not carried out so completely as with the β-naphthol dyes, observations being made on only the more important physical constants. The absorption spectra were determined throughout the visible and ultraviolet to a frequency of 1360. These data which are given in Fig. 1 confirm the fact that the absorption

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[10] Ingersoll, THIS JOURNAL, 47, 1168 (1925).

spectra of optical enantiomorphs are the same, a point which previous to the work on the β-naphthol dyes of this series had not been definitely confirmed for both of the enantiomorphic forms. The curve obtained from the absorption-spectra observations did not follow so closely the curve of dimethylaniline-azobenzene as the β-naphthol dye did that of the absorption spectra of benzene-azo-β-naphthol. This might have been expected, as the naphthol group is acidic and the addition of an extra acidic group in the form of phenylamino-acetic acid would cause less change than the addition of the acidic group to the basic dye derived from dimethylaniline.

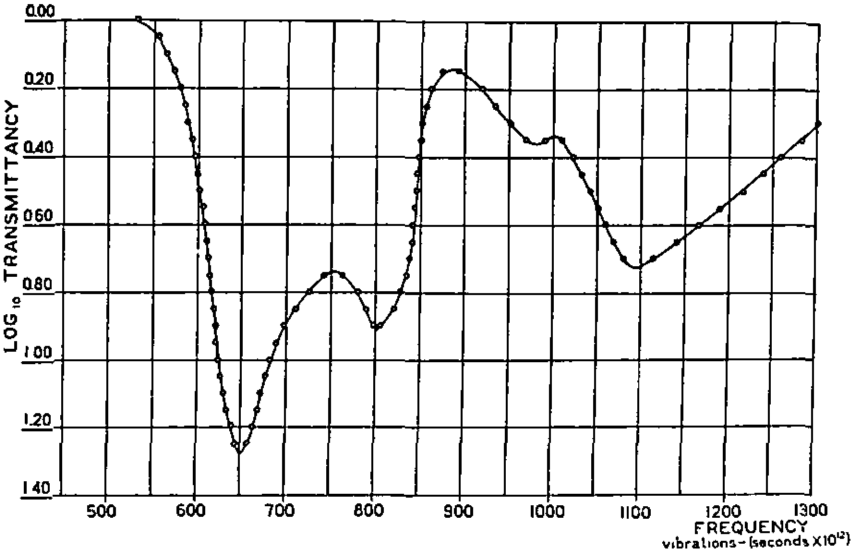

Fig. 1.—The absorption spectrum of *dl*-phenyl(*p*-dimethyl-aminobenzene-azobenzoylamino) acetic acid in alcohol. Concn., 0.01 × 25 g. per liter; cell thickness, 1 cm. The absorption-spectra curves of the *l* and *d* forms were also determined and found to be identical within the allowable experimental deviations.

The rotation of the dimethylaniline dyes, while normal, was different from the β-naphthol rotation in that the rotatory-dispersion curve crossed the 0° axis and hence changed in sign. This is a common occurrence in rotatory-dispersion curves, but gave considerable difficulty and trouble at first due to the fact that the original rotation measurements were made by using sunlight as a light source and this heterogeneous light source gave a 0° rotation for both forms. The dyes in all other respects behaved as optical pairs should. By the use of monochromatic light, however, it was possible to observe rotations on these dyes, which in the case of the *d*-dye was positive on the longer wave-length side and negative on the shorter wave-length side, and *vice versa* for the *l*-dye (Fig. 3).

The rotatory-dispersion curves of a number of the active intermediates used in this work have been determined and are given in Fig. 2. The concentrations of the solutions used in these curves are the same as those used by Ingersoll and Adams.[2a] The observations on the absorption spectra in the visible were made on Koenig, Martens, and Keuffel and Esser spectrophotometers and in the ultraviolet on a Hilger sector photometer. The rotational measurements were made on a Franz Schmidt and Haensch polarimeter.

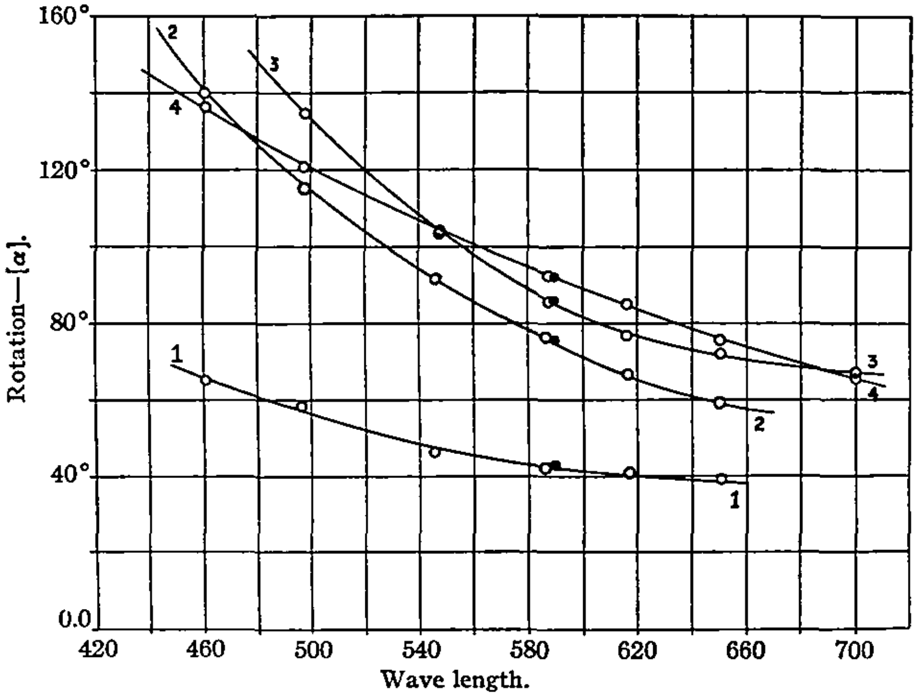

Fig. 2.—The rotatory-dispersion curves of the intermediate active products used in the preparation of these dyes. These observations were taken on the *l* compounds as follows; (1) *d*-camphor-sulfonate salt of *l*-phenylamino-acetic acid (3.8364 g. made up to 50 cc. with 34.54 cc. of *N* hydrochloric acid and the remainder water; 0.4177 g. in 20 cc. of water at 20°); (2) *l*-phenylamino-acetic acid, values given are $\alpha/2$; (3) *l*-phenyl(*p*-nitrobenzoylamino)acetic acid (2.000 g. in 25 cc. of absolute alcohol at 20°); (4) *l*-phenyl(*p*-aminobenzoylamino)acetic acid (2.000 g. in 25 cc. of *N* hydrochloric acid at 20°). The black dots represent the values for these same compounds as prepared and observed by Ingersoll.[2]

Dyeing Experiments.—The wool cloth used in the dyeings was material from the Bureau of Standards dye laboratory employed particularly for standard dyeings. It was of very high purity. The silk was unweighted material from the same source. The dyeings were made in a standard dye vat consisting of porcelain cups all immersed in the same heating bath. Dyeings were made for the same length of time, allowed to drain for the same time and then carefully washed. The remaining solution was titrated with titanous chloride according to the method of Calcott and English.[6b]

The dyeing experiments were made at high temperatures (95°) rather than at the low temperatures (20°) used in other similar experiments by other observers,[8,9] because it was felt that if a chemical action did take place it would be accelerated at higher temperatures. Observations of other investigators have definitely shown that for most dyes there is a physical adsorption of dyes by fibers at low temperatures which is more or less reversible and that at higher temperatures the amount of dye adsorbed is increased. There appears to be a different relation existing between the dye and the fiber at the higher temperature which is not so reversible as that found in dyeings at lower temperatures.

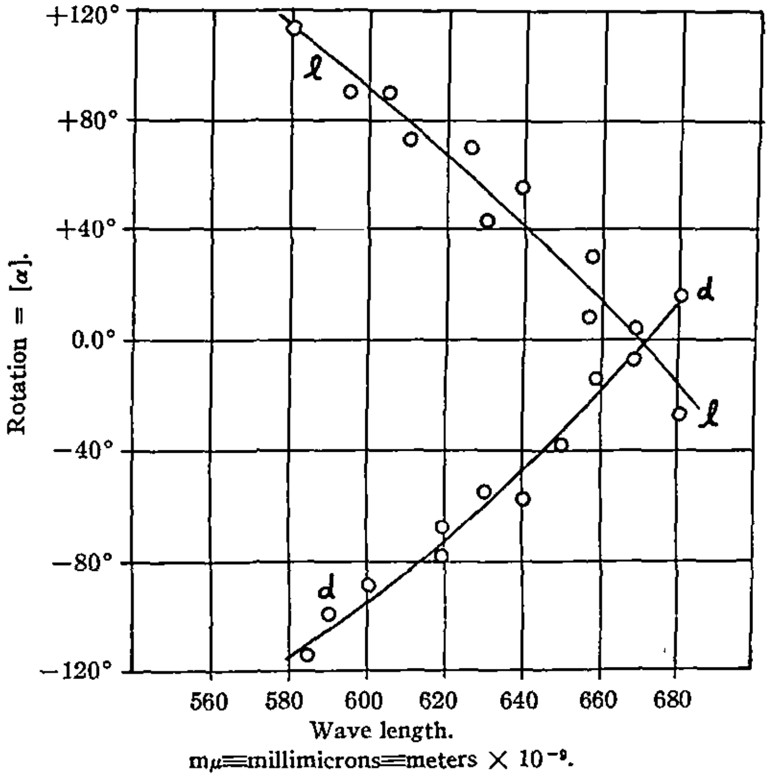

Fig. 3.—The rotatory-dispersion curves of *d*- and *l*-phenyl(*p*-dimethylaminobenzene-azobenzoylamino)acetic acid in ethyl acetate; concn., 1.000 g. per liter.

The dye solutions used in these dyeing experiments were prepared as follows.

For the β-naphthol dyes, 0.4000 g. of the dye was dissolved in a solvent consisting of 40 cc. of 95% alcohol and 160 cc. of water to which had been added 0.100 g. of anhydrous sodium sulfate and 0.075 g. of anhydrous sodium carbonate. For the dimethylaniline dyes, 0.4000 g. of the dye was dissolved in 100 cc. of 95% alcohol and 100 cc. of water to which had been added 0 100 g. of anhydrous sodium sulfate and 0.100 g. of sodium acid sulfate. The time and temperature for all the dyeing experiments were, respectively, 30 minutes and 95° (Table I).

Table I

Dyeing Experiments

40 cc. of dye solution containing 0.0800 g. of dye was used in each experiment.

β-Naphthol Dyeings

Dye	$TiCl_3$ Titrations Blank soln., g.	Part. exhausted soln., g	Dye adsorbed, %
	A. Wool, 2.000 g.		
d	0 0799	0.0308	61.45
l	.0798	.0302	62.15
dl	.0795	.0266	66.55
	B. Silk, 1.000 g.		
d	0.0799	0.0315	60.58
l	.0798	.0310	61.13
dl	.0795	.0274	65.52
	Dimethylaniline Dyeings		
	A. Wool, 2.000 g.		
d	0.0809	0.0331	59.08
l	.0785[a]	.0318[a]	59 45
dl	.0801	.0298	62.83
	B. Silk, 1.000 g.		
d	0.0809	0.0364	55 00
l	.0785[a]	.0352[a]	55.15
dl	.0801	.0338	57.85

[a] The consistent difference in both the blank run and the partially exhausted dye solutions with the values for the *d*-dyeings indicates that the dye solution was slightly weak and a correction for this difference would make the exhausted wool value 0.0326 and the exhausted silk value 0.0359. Dyes of this type are known to adsorb moisture readily on long exposure to air; the sample used had been prepared for some time.

The partially exhausted liquors from the dyeings of the racemic dyes with wool and silk were examined with a polarimeter with monochromatic light of various wave lengths and no rotation could be detected in either the β-naphthol or dimethylaniline dye solutions. The polarimeter used in these observations was capable of being read to 0.0002° with accuracy and was of the best design and construction.

Samples of these dyeings were examined spectrophotometrically by studying their reflection spectra and, while the height of the curve is not directly proportional to the concentration of the dye in the sample, the results showed that the racemic form is slightly stronger than the active forms and that the two active dyeings are of the same intensity.

Tests were also made on the dyed samples as to their fastness to light. The dyes were very fast to light and required over 200 hours' exposure to a violet-carbon arc to cause noticeable fading, and then no difference could be detected in the rates of fading of the active or racemic dyeings.

Benzene-azosalicylaldehyde-α(β-naphthol)benzylamine, III.—A solution of 11.3 g. of benzene-azosalicylaldehyde[11] in 100 cc. of alcohol and a solution of 12.4 g. of

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[11] Tummeley, *Ann.*, 251, 174 (1889).

α-(β-naphthol)benzylamine[12] in an equal amount of alcohol were mixed together while hot. On cooling, the brilliant yellow-orange dye separates; m. p, 210–212°. It is quite soluble in benzene, slightly soluble in alcohol, insoluble in water or alkaline solutions.

Anal. Subs., 0 1147, 0.1112. Calcd. for $C_{30}H_{23}O_2N_3$: C, 78.7; H, 5.03. Found: C, 78.3, 78.6; H, 5.64, 5.24.

The active modifications of this dye have been prepared and have a somewhat higher melting point than the racemic modification (220–225°) and at a wave length of 610 mμ gave a rotation of about 80° in a benzene solution. The work on these active dyes is not completed and the purity of the active modifications has not been definitely established. They are unsatisfactory for dyeing experiments due to their low solubility. It is hoped that some derivatives of this type may be obtained which will give solutions from which comparative dyeings may be made.

Summary

1. The active isomers of optically active dyes have the same physical properties, including adsorption by inert and active materials, adsorption, color, fastness to light, melting points and all other physical properties tested.
2. The rotatory-dispersion curves of these active dyes and of the intermediates used have been studied and found to be normal.
3. A new type of asymmetric dye has been prepared from an asymmetric derivative of benzylamine.
4. No apparent difference in adsorption of the two active forms could be detected in the dyeing experiments on these dyes.
5. The racemic dyes appear to be adsorbed to a greater extent than the active dyes, by both inactive and active adsorbing agents.

URBANA, ILLINOIS

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[12] Betti, *Gazz. chim. ital.*, [ii] 50, 301, 310 (1900), and subsequent articles in the same journal.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

OPTICALLY ACTIVE DYES. IV. ASYMMETRIC DYES FROM META-AMINOMANDELIC ACID

BY WALLACE R. BRODE[1] WITH ROGER ADAMS

RECEIVED MAY 24, 1926 PUBLISHED AUGUST 5, 1926

In continuation of the work of Porter and Hirst,[2] Porter and Ihrig[3] have prepared a number of asymmetric dyes among which were the phenol and β-naphthol derivatives of diazotized *m*-aminomandelic acid. With the β-naphthol dyes they carried out dyeing experiments which led them to conclude that a chemical reaction was involved in the dyeing process. The work of Brode with Adams[4] in the previous paper has shown that in the case of asymmetric dyes derived from phenylamino-acetic acid there is no selective absorption or other indication of chemical action in the mechanism of dyeing. Inasmuch as the results obtained by Porter and Ihrig on the mandelic acid dyes were in contradiction to these, it was deemed advisable to repeat the experiments on the mandelic acid dyes.

The preparation of *m*-aminomandelic acid was through the *m*-nitromandelic acid and the dyes were then synthesized following the directions of Porter and Ihrig. The melting points obtained were as follows: *dl*-β-naphthol dye, 205–206° (no melting point was given in the publication by Porter and Ihrig but in a private communication Ihrig gave it as 206.5°); the *dl*-phenol dye, 120–121° (Porter and Ihrig gave 119°). Analysis by the titanous chloride method confirmed the identities of these.

The same directions were used in the dyeing experiments that were previously used in the tests by Porter and Ihrig on the same dyes. Duplicate tests were made and the experiments performed on the phenol dye as well as on the β-naphthol dye. One g. of the racemic dye was dissolved in 75 cc. of glacial acetic acid and this was treated with 2.5 g. of wool for 24 hours at 20°. The solution was then filtered, 20 cc. removed for polarimetric observation and the remainder again treated with 2.5 g. of wool under the same conditions for another 24 hours and then filtered, a sample removed and the process again repeated. The dyeing experiments were made by the use of wool flock,[5] a method which gives a much more uniform and greater adsorption than the skein method of dyeing. Wool samples were also treated in acetic acid solutions containing no dye and, after treatment in which the time and temperature were maintained as in the previous experiments, the rotation of these solutions was also measured.

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[1] This communication is an abstract of a portion of a thesis submitted by Wallace R. Brode in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Porter and Hirst, THIS JOURNAL, **41**, 1264 (1919).

[3] Porter and Ihrig, *ibid.*, **45**, 1990 (1923).

[4] Brode with Adams, *ibid.*, **48**, 2193 (1926).

[5] Appel, *Am. Dyestuff Reporter*, **13**, 507 (1924).

These dyeing experiments and the rotational measurements were made at the Bureau of Standards.[6] The observations were made at a wave length of approximately 585 mμ for the colorless and phenol dye solutions, and at about 610 mμ for the naphthol dye solutions. The naphthol dye being a dark red as compared with the yellow color of the phenol dye, it was necessary to use a shorter cell in order to allow enough light to pass through to obtain accurate readings. In the case of the naphthol dye, a 3 cm. cell was used and for the phenol dye a 10 cm. cell. The polarizing angle of the separate Nicol prisms in the polarizer could, of course, be made very small in the case of the clear and phenol-dye solutions, but it had to be much larger in the case of the naphthol dye in order to allow sufficient light to pass through; hence, a greater allowable variation exists in these latter measurements.

The readings recorded below are the average of a number of observations on each solution and in each case the observed rotation is well within the allowable experimental error. In other words, no rotation was observed in any of the solutions.

Solution	Angles of rotation, ° 0 hrs.	24 hrs.	48 hrs.	72 hrs.
Phenol dye (10cm. tube)	+0.012	+0.021	+0.005	−0.006
β-Naphthol dye (3cm. tube)	+ .006	+ .004	− .008	+ .001
β-Naphthol dye (Porter and Ihrig)	....	− .66	− .91	....

Porter and Ihrig did not publish the tube length used in their polarimetric observations so that it was impossible to verify their data or to reproduce exactly the conditions of their measurements. The concentration of the solution, however, is known, and from experiments made with dye solution of this concentration no satisfactory readings could be made in a 20 cm. cell, since the amount of light that passed through was so small as to require a rather large polarizing angle, thus introducing considerable observational error in the readings. No apparent rotation was observed in acetic acid solutions which had been treated with wool, as evidenced by the reading of +0.004 which was obtained when wool was allowed to stand in acetic acid for 72 hours before being filtered off.

The dyed wool that was filtered off at the end of the first 24 hours should have contained optically active dyes if the theory of Porter and Ihrig is correct. This wool was, therefore, allowed to stand for 48 hours in acetic acid and, after the liquid had been separated by filtering, the rotation of the solution, which had extracted the larger portion of the dye from the fibers, was observed. In the case of the phenol dye, a rotation of —0.001° was observed and in the case of the β-naphthol dye a rotation of +0.003°

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[6] The authors are indebted to the Polarimetric Section of the Bureau of Standards for the use of their apparatus and to Mr. F. P. Phelps for assistance in making these measurements.

was observed, both within the experimental error of the apparatus, considering the fact that the solutions were colored.

Absorption Spectra

In order further to identify and distinguish these dyes, their absorption spectra in the visible and ultraviolet portions of the spectrum were determined. These observations were made in two solvents, namely, alcohol and 3% aqueous sodium hydroxide. These data are presented in Figs. 1 and 2 using the same method of plotting and notation as in previous papers of this series.[7]

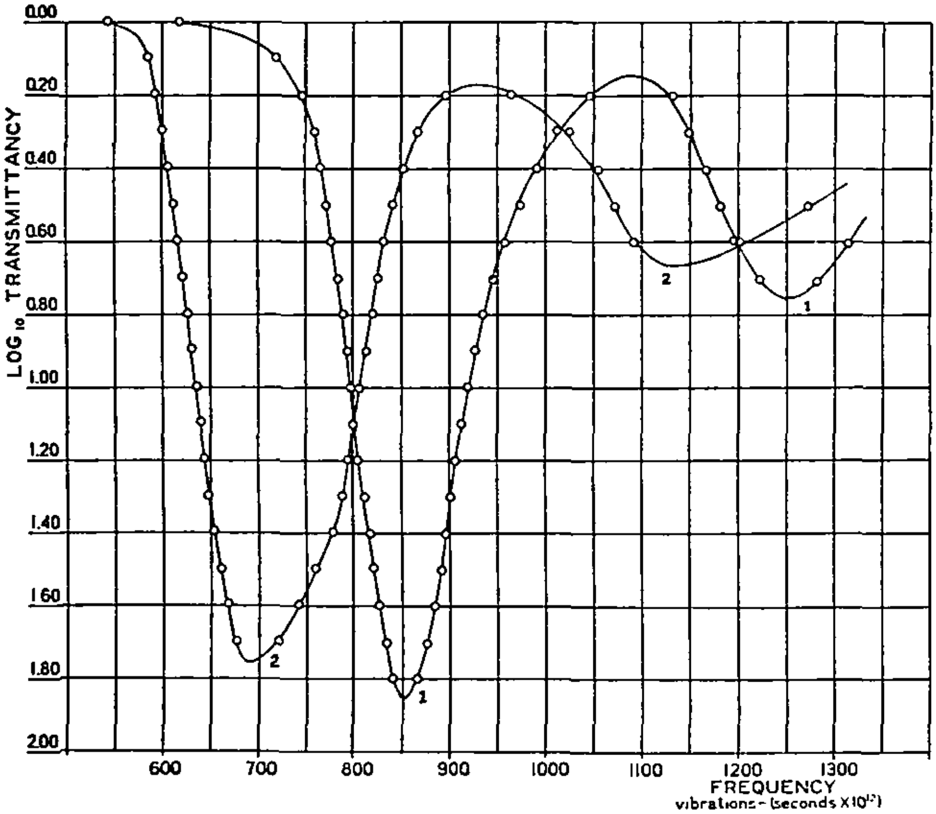

Fig. 1.—The absorption spectra of *dl-m*-azophenolmandelic acid in alcohol (1) and in 3% aqueous sodium hydroxide (2); concn., 0.04 × 576 g. per liter; cell thickness, 0.5 cm.

Experimental Part

***m*-Nitromandelic Acid.**—Much difficulty was encountered in this preparation and consequently details are given.

A solution of 30 g. of *m*-nitrobenzaldehyde (m. p., 34°) in 90 cc. of glacial acetic acid was placed in a round-bottomed flask fitted with a mechanical stirrer and was cooled to 0°. At this temperature the mixture was a mush, due to the solidification

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[7] Brode with Adams, This Journal, 46, 2032 (1924).

of the acetic acid. To this, during constant stirring, was added 15 g. of potassium cyanide dissolved in a minimum amount of water, about 30 cc. This gave a yellow or greenish pasty mass which was stirred continuously for about four or five hours. After the reaction had been started no more ice was added to the ice-bath and after three or four hours the solution warmed to 8–10° and was of a clear, straw-yellow color. The solution was treated with sodium carbonate, extracted with ether and the ether was removed by evaporation on a steam-bath, care being taken not to heat the liquid cyanohydrin after the ether had been removed. The cyanohydrin was then treated with 150 cc. of concd. hydrochloric acid. This solution, which was still a light yellow, was evaporated on a steam-bath nearly to dryness, more hydrochloric acid added and the evaporation continued. The resulting mush was extracted with ether and about 10 g. of ammonium chloride filtered off from the ether solution. The ether solution was evaporated on a steam-bath to a small volume and the evaporation continued in a vacuum desiccator. On standing for a short time, the viscous liquid solidified to give a light yellow, crystalline solid which crystallized from benzene, and the hot benzene on cooling precipitated light yellow plates of *m*-nitromandelic acid; m. p., 118° (Heller[8] gives 119°). The yields varied widely but averaged about 40–50%.

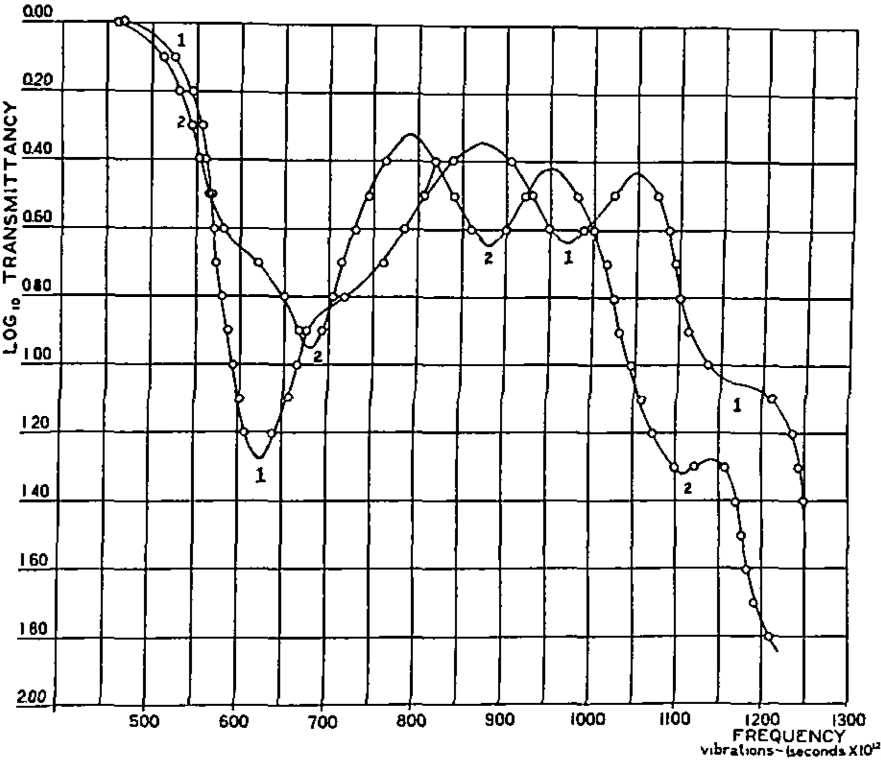

Fig. 2.—The absorption spectra of *dl-m*-azo-β-naphtholmandelic acid in alcohol (1) and in 3% aqueous sodium hydroxide (2); concn., 0.05 × 376 g. per liter; cell thickness, 0.5 cm.

The reduction was carried out as described by Porter and Ihrig and the resulting amine diazotized and coupled to β-naphthol and phenol.

***dl-m*-Azo-β-naphtholmandelic acid**, $OH.C_{10}H_6.N:N.C_6H_4\ CHOH.COOH$.—This is a

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[8] Heller, *Ber.*, **46**, 3976 (1913).

dark red dye, crystallizing in rosets, m. p. 205–206° (Ihrig gives 206 5°), soluble in alcohol, benzene and ether, and less soluble in acetic acid (a solution of 1 g. in 75 cc., on standing in a closed container, will deposit a large amount of the crystalline solid).

Anal. —N=N—. Calcd.: 8.7. Found: 8.6, 8.8 (by $TiCl_3$ titration).

dl-m-**Azophenolmandelic acid,** $HO.C_6H_4.N:N.C_6H_4.CHOH.COOH$.—This is a light yellow dye, crystallizing in plates, m. p. 119–120° (Porter and Ihrig give 119°), soluble in alcohol, benzene and in acetic acid, and slightly soluble in water.

Anal. Calcd.: —N=N—, 10.33. Found: 10.30, 10.26 (by $TiCl_3$ titration).

Summary

Two asymmetric dyes, as previously prepared by Porter and Ihrig, have been synthesized.

The absorption spectra of these dyes in various solvents have been determined.

Dyeing experiments have been made with these dyes and the results from these tests have failed to confirm the previous results obtained by Porter and Ihrig. No rotation was observed in any of the solutions examined and no evidence has been obtained which would indicate the selective adsorption of one of the enantiomorphic forms of the racemic dye.

These data agree with previous data obtained by the authors and afford additional proof that the dyeing mechanism is not necessarily a chemical phenomenon.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

THE CHEMICAL PROPERTIES OF CAPROYLRESORCINOL AND SOME OF ITS DERIVATIVES

BY D. TWISS

RECEIVED MAY 27, 1926 PUBLISHED AUGUST 5, 1926

Johnson and Lane,[1] and recently Leonard,[2] have announced that certain alkyl resorcinols and especially hexylresorcinol possess high bactericidal strength as compared to phenol, and that these derivatives are relatively non-toxic. Considerable interest has been developed in applying these compounds to the problem of internal antisepsis. A large number of alkyl resorcinols as well as acyl resorcinols, the products from which they are derived, have been made in the laboratories of Sharp and Dohme, Baltimore; the acyl resorcinols by condensing fatty acids with resorcinol by means of zinc chloride, the alkyl resorcinols by reducing these ketones by the method of Clemmensen,[3] which has already been applied by Johnson and Lane to the lower members of this series.

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[1] Johnson and Lane, THIS JOURNAL, 43, 348 (1921).

[2] Leonard, *J. Am. Med. Assoc.*, 83, 2005 (1924).

[3] Clemmensen, *Ber.*, 46, 1837 (1913).

However, at the present time little is known about the chemistry of the alkyl and acyl resorcinols, and it was therefore considered worth while to study the chemistry of one member of each series, namely, hexylresorcinol and caproylresorcinol.

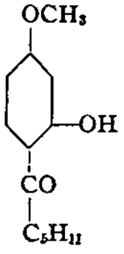
As is shown in this paper, acyl resorcinols may also be obtained by condensing the esters of the fatty acids with resorcinol. For example, caproylresorcinol (resorcyl-amyl ketone) is formed when ethyl caproate and resorcinol are heated together in the presence of zinc chloride. As a condensing agent zinc chloride proved to be superior to sulfuric acid, phosphorus pentoxide and aluminum chloride or mixtures of zinc chloride and aluminum chloride. Attempts to reduce partially the caproylresorcinol in various reducing media, in order to obtain the secondary alcohol, resorcyl-amyl carbinol, did not yield positive results. Thus it was found that the ketone was not reduced at all by aluminum amalgam in acid, neutral or alkaline solution, nor by zinc powder and alcoholic sodium hydroxide. Reduction with sodium in absolute alcohol resulted in the formation of a product of high molecular weight, which dissolved in sodium hydroxide to give a dark red coloration.

It may be desirable to point out that a large difference in chemical reactivity exists between the compounds hexylresorcinol and caproylresorcinol. There are two reasons for this: first, the difference in intensity of the steric-hindrance effect between the hexyl group in the former and the caproyl group in the latter, on the hydroxyl group in the *ortho* position to these substituents, and second, the stronger stabilizing effect of the negative caproyl group on the benzene ring as compared with that of the neutral hexyl group.

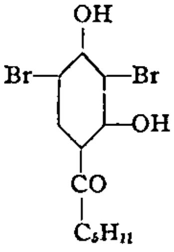
The first reason is clearly indicated by the different behavior of the two compounds on methylation. Whereas caproylresorcinol gives only the monomethyl ether, even when methylated with an excess of dimethyl sulfate or methyl iodide, hexylresorcinol gives readily mono- or dimethyl ether according to the amount of methylating agent used. Furthermore, the monomethyl ether of the ketone forms an insoluble, white, flaky sodium salt when shaken with concd. aqueous sodium hydroxide, while the monomethyl ether of the reduced compound is soluble in sodium hydroxide solution. Direct action of acetyl chloride without the addition of a solvent gives a mono-acetate in the case of the ketone and a diacetate in the case of hexylresorcinol. It was remarked that caproylresorcinol dissolves in acetyl chloride without the evolution of hydrogen chloride to give a dark red solution, and with considerable absorption of heat. The reaction begins after heating, while the color changes to yellow. When acetyl chloride is added to hexylresorcinol the evolution of hydrogen chloride begins immediately. Benzoylation according to Schotten-Baumann with *p*-nitrobenzoyl chloride gives a crystalline monobenzoate with the ketone. Benzoylation of hexylresorcinol with benzoyl chloride, *p*-nitrobenzoyl chloride, or 1,3-dinitrobenzoyl chloride results in the formation of non-crystallizable or tarry products.

The second reason, the stabilization of the benzene ring by the caproyl group, is clearly shown by the behavior of the two compounds on nitration or bromination. Caproylresorcinol gives a crystalline mononitro derivative, but hexylresorcinol is completely destroyed by nitric acid. Bromination of the ketone in glacial acetic acid gives a crystalline dibromo derivative, but hexylresorcinol forms an oily dibromo compound which splits off hydrogen bromide on standing. Attempts to transform this product into a stable crystalline derivative through methylation or benzoylation were not successful, as only non-crystallizable oils were obtained. An attempt to oxidize nitro- and dibromocaproylresorcinol to benzoic acid derivatives, in order to determine the positions of the bromine atoms, led to the complete alteration of the compounds. This also occurred with the monomethyl ether. The reason for this is probably that the caproyl group splits off and regenerates caproic acid, as was found to be the case with caproylresorcinol itself, and with its monomethyl ether when fused with potassium hydroxide. According to Dahse,[4] dibromoresacetophenone is more resistant toward oxidizing agents because of the stronger acidity of the acetyl group. It gives 2,4-dibromo-1,3-dihydroxybenzoic acid when oxidized with chromic acid in glacial acetic acid, and when oxidized with nitric acid dinitrobromo-dihydroxybenzoic acid is formed.

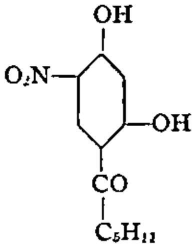
A direct proof of the constitution of the three caproylresorcinol derivatives could not be obtained. It is evident, however, that in the monomethyl ether the methyl group is attached to the hydroxyl in the *para* position to the caproyl group (Formula I).



I



II



III

This must also be assumed for the monoacetate and the *p*-nitromonobenzoate. The position of the two bromine atoms in dibromocaproylresorcinol (II) must be analogous to that of the bromine atoms in dibromoresacetophenone, determined by Dahse. That is to say, one bromine atom must be *ortho* to both hydroxyl groups, and the second *ortho* to one and *para* to the other hydroxyl group. The nitro group in nitrocaproylresorcinol (III) is probably *ortho* to one and *para* to the other hydroxyl group.

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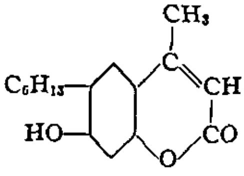
[4] Dahse, *Ber.*, **41**, 1623 (1908).

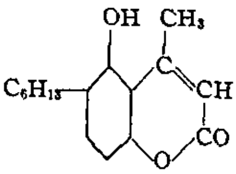
Nencki and Sieber[5] prepared a mononitro derivative of resacetophenone, but made no statements as to the position of the nitro group.

According to Tahara,[6] resacetophenone on treatment with acetic anhydride and anhydrous sodium acetate gives a small amount of a coumarin along with other products. Coumarin formation was also observed by Komarowsky and Kostanecki[7] when benzoylresorcinol was treated in a like manner. When, however, caproylresorcinol is treated with acetic anhydride and anhydrous sodium acetate, no formation of coumarin is observed. The reaction yields a thick black oil from which only a small amount of caproylresorcinol diacetate could be isolated. On treating hexylresorcinol with aceto-acetic ester in sulfuric acid solution a substituted coumarin results. Of the two possible isomers, IV and V, V must be eliminated as there is no evidence that the formation of the coumarin nucleus takes place between the two hydroxyl groups.



4-methyl-6-hexyl-7-hydroxycoumarin

IV



4-methyl-6-hexyl-5-hydroxycoumarin

V

Both caproylresorcinol and hexylresorcinol show an abnormal cryoscopic behavior. A preliminary investigation showed that they form several addition compounds with benzene as well as with nitrobenzene, the exact nature of which has not yet been determined.

Experimental Part

Caproylresorcinol.—Fifty-five g. of resorcinol was dissolved in 72 g. of ethyl caproate, 34 g. of zinc chloride was added and the mixture was heated and stirred for one hour at its boiling point. The reaction product was washed with water and was distilled in a vacuum. Forty-five g. of ester was recovered and 24 g. of ketone was obtained. The yield was 60% calculated on the basis of ester actually used.

Anal. Subs., 0.2163, 0.1440: CO_2, 0.5471, 0.3639; H_2O, 0.1493, 0.0989 Calcd. for $C_{12}H_{16}O_3$: C, 69.19; H, 7.69. Found: C, 68.98, 68.92; H, 7.55, 7.63.

The white crystals melt at 56–57°, and boil at 217–218° under 14 mm pressure and at 343–345° under atmospheric pressure, with decomposition. Caproylresorcinol is soluble in alkali, sodium carbonate, borax and all ordinary organic solvents except petroleum ether. It also dissolves in concd. sulfuric acid from which it can be precipitated again unchanged by water, but sulfonation takes place on long standing in this solvent. The crystals become brown on long exposure to light and give a red coloration with ferric chloride in alcohol or water.

MONOMETHYL ETHER.—In 50 cc. of 20% sodium hydroxide solution was dissolved 20.8 g. of ketone, and while the solution was shaken vigorously, 20 cc. of dimethyl

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[5] Nencki and Sieber, *J. prakt. Chem.*, [2] **23**, 150 (1881).

[6] Tahara, *Ber.*, **25**, 1304 (1892).

[7] Komarowsky and Kostanecki, *Ber.*, **27**, 1997 (1894).

sulfate was added in several portions. The resulting oil was dissolved in benzene, dried with calcium chloride and distilled in a vacuum. The monomethyl ether was obtained as a colorless oil, boiling at 189–192° (12–13 mm.); yield, 16 g., or 72%.

Anal. Subs., 0.2002: CO_2, 0.5158; H_2O, 0.1439. Calcd. for $C_{13}H_{18}O_3$: C, 70.26; H, 8.13. Found: C, 70.36; H, 7.99.

In alcoholic solution the substance gives a red coloration with ferric chloride. It is insoluble in dil. sodium hydroxide solution, and when shaken with concd. sodium hydroxide solution gives white flakes of the insoluble sodium salt. Unlike caproylresorcinol itself, the monomethyl ether shows normal cryoscopic behavior.

Mol. wt. Subs., 0.4483, 0.6387: benzene, 12.55; Δt, 0.899°, 1.124°. Calcd. for $C_{13}H_{18}O_3$: mol. wt., 222. Found: 221, 226.

As a by-product, a very small amount of white crystals was obtained; m. p., 35–36°. This substance gives no coloration with ferric chloride in alcoholic solution. It is probably the dimethyl ether of caproylresorcinol.

OXIME.—Ten g. of caproylresorcinol was dissolved in 50 cc. of absolute alcohol and the solution boiled for five hours with 4 g. of hydroxylamine hydrochloride and 5.8 g. of anhydrous potassium acetate. The oxime crystallized after the solution had been concentrated. Upon recrystallizing from 50% alcohol, white crystals melting at 190–191° with decomposition were obtained; yield, 7 g., or 65%.

Anal. Subs., 0.7243, 0.5369: cc. of 0.1 *N* NH_3, 30.63, 23.53. Calcd. for $C_{12}H_{17}NO_3$: N, 6.13. Found: 5.92, 6.14.

The oxime is insoluble in water and gives a dark blue-violet coloration in alcoholic solution with ferric chloride.

p-NITROBENZOYL ESTER.—In a solution of 8 g. of sodium hydroxide in 60 cc. of water was dissolved 20.8 g. of caproylresorcinol, and 37 g. of finely powdered *p*-nitrobenzoyl chloride was added in several portions. The mixture was shaken vigorously. The oil that separated solidified to a crystalline mass on cooling. Recrystallized from alcohol, pale yellow crystals were obtained; m. p., 89–91°; yield, 20 g., or 56%.

Anal. (Kjeldahl, with addition of zinc powder). Subs., 0.5795, 0.5714: cc. of 0.1 *N* NH_3, 17.26, 17.26. Calcd. for $C_{19}H_{19}NO_6$: N, 3.92. Found: 4.17, 4.23.

MONOACETATE.—To 20.8 g. of ketone was added 15.6 g. of acetyl chloride. The ketone gradually dissolved, and during heating on the water-bath hydrogen chloride was evolved. The reaction product was poured into water, the oil dissolved in benzene, dried with sodium sulfate and distilled in a vacuum. The colorless oil boiled at 213–215° (14 mm.); yield, 19 g., or 76%.

Anal. Subs., 0.2047: CO_2, 0.5066; H_2O, 0.1365. Calcd. for $C_{14}H_{18}O_4$: C, 67.16; H, 7.25. Found: C, 67.49; H, 7.41.

Dissolved in alcohol, the substance gives a red coloration with ferric chloride. No solid oxime can be obtained from the monoacetate.

DIACETATE.—A poor yield of the diacetate was obtained by boiling the ketone with anhydrous sodium acetate and acetic anhydride for several hours. Much tar was formed in the reaction. From the thick black oil thus formed the diacetate was obtained as a thick yellow oil boiling at 229–232° (13 mm., with some decomposition). Saponification with alcoholic sodium hydroxide regenerated the ketone.

MONONITRO DERIVATIVE.—Forty cc. of nitric acid (d., 1.4) was poured over 10 g. of powdered ketone. After a vigorous reaction had taken place the liquid was poured into water. The oil that separated soon solidified. After several crystallizations from alcohol the substance appeared as almost white, glistening plates; m. p., 73–74°; yield, 6.3 g., or 52%.

Anal. (Kjeldahl, with addition of zinc powder). Subs., 0.5456, 0.5283: cc. of 0.1 *N* NH_3, 21.33, 20.09. Calcd. for $C_{12}H_{15}NO_5$: N, 5.53. Found: 5.47, 5.32.

The nitro compound is slightly soluble in cold alcohol, dissolves in sodium hydroxide with development of a yellow color and gives a dark red color with ferric chloride in alcoholic solution.

DIBROMO DERIVATIVE.—Thirty-two g. of bromine (10.1 cc.) dissolved in 50 cc. of glacial acetic acid was added gradually to a solution of 20.8 g. of ketone in 50 cc. of glacial acetic acid. The reaction took place immediately with evolution of hydrogen bromide and was terminated by heating on a water-bath at 40–50° for a short time. The solution was then poured into cold water and the oil that separated solidified to a brown crystalline mass. It was pressed on a porous plate and was crystallized from 75% alcohol. Twelve g. of pale yellow needles was obtained; m. p., 102–103°; yield, 33%.

Anal. Subs., 0 2727: AgBr, 0.2818. Calcd. for $C_{12}H_{13}O_3Br_2$: Br, 43.68. Found: 43.98.

Hexylresorcinol.—Fifty g. of caproylresorcinol was reduced at boiling temperature, while the liquid was stirred vigorously, for six to eight hours with 125 g. of amalgamated zinc and 300 cc. of concd. hydrochloric acid diluted with 200 cc. of water. The resulting oil was distilled in a vacuum; yield, 35.5 g. of hexylresorcinol, or 76%.

Anal. Subs., 0.1301, 0.1172: CO_2, 0.3545, 0.3186; H_2O, 0.1100, 0 0976. Calcd. for $C_{12}H_{18}O_2$: C, 74.23; H, 9.28. Found: C, 74.30, 74.14; H, 9.39, 9.25.

Hexylresorcinol crystallizes from benzene in white needles and from ligroin in shining white plates; m. p., 67–68°; b. p., 198–200° at 13–14 mm. and 333–335° at atmospheric pressure. The decomposition of hexylresorcinol boiling under atmospheric pressure is less than that of the ketone. The crystals become brown on long exposure to light. The compound is soluble in all ordinary organic solvents except petroleum ether. It is, furthermore, soluble in alkali, sodium carbonate, borax and concd. sulfuric acid. From the last it may be precipitated unchanged on diluting with water. However, long standing in concd. sulfuric acid causes sulfonation. The solubility in water is 1:2000. In alcoholic solution hexylresorcinol gives a green coloration with ferric chloride.

DIMETHYL ETHER.—In 100 cc. of 20% sodium hydroxide solution was dissolved 19.4 g. of hexylresorcinol, and 40 cc. of dimethyl sulfate was added gradually. The mixture was shaken vigorously and the oil that separated was dissolved in ether, dried with calcium chloride and distilled in a vacuum. The colorless oil thus obtained boiled at 164–165° under 12 mm. pressure; yield, 15 g., or 72%.

Anal. Subs., 0.1048: CO_2, 0.2912; H_2O, 0 0937. Calcd. for $C_{16}H_{22}O_4$: C, 75.96; H, 9.98. Found: C, 75.78; H, 9.93.

The dimethyl ether as well as the monomethyl ether shows normal cryoscopic behavior.

Mol. wt. Subs., 0.2064, 0.3594: benzene, 11.88; Δt, 0.403°, 0.707°. Calcd. for $C_{14}H_{22}O_2$: mol. wt., 222. Found: 216, 214.

The dimethyl ether is insoluble in alkali and gives no coloration with ferric chloride in alcoholic solution. The monomethyl ether is obtained as an alkali-soluble, colorless oil when hexylresorcinol is treated with the calculated amount of dimethyl sulfate.

DIACETATE.—Ten g. of hexylresorcinol was mixed with 25 g. of acetyl chloride. The hexylresorcinol gradually dissolved with evolution of hydrogen chloride. The reaction was terminated by heating on a water-bath. The reaction product was poured into water, washed with sodium bicarbonate solution, dissolved in benzene, dried with sodium sulfate and distilled in a vacuum. Twelve g. of colorless oil was obtained; b. p., 198–199° (15 mm.); yield, 84%.

Anal. Subs., 0.2103, 0.2206: CO_2, 0.5338, 0.5578; H_2O, 0.1498, 0.1580. Calcd. for $C_{16}H_{22}O_4$: C, 69.02; H, 7.97. Found: C, 69.23, 68.96; H, 7.92, 7.96.

Coumarin.—In 13 g. of aceto-acetic ester was dissolved 19.4 g. of hexylresorcinol, and solution was slowly added to 400 g. of cold, 82% sulfuric acid. The mixture was left for 24 hours and then poured onto ice. The sticky substance that separated gradually solidified. It was washed several times with water and was crystallized from alcohol. Ten g. of pure substance was obtained; m. p., 165°; yield, 39%.

Anal. Subs., 0.1207, 0.1116: CO_2, 0.3254, 0.3014: H_2O, 0.0836, 0 0773. Calcd. for $C_{16}H_{20}O_3$: C, 73.85; H, 7.75. Found: C, 73.53, 73.65; H, 7.70, 7.60.

My thanks are due to Mr. L. C. Copeland for his assistance with several of the preparations.

Summary

1. Caproylresorcinol was prepared by the condensation of ethyl caproate with resorcinol.
2. A comparative study was made of the behavior of caproylresorcinol and of hexylresorcinol with regard to methylation, reaction with acid chlorides, nitration, bromination and formation of coumarin.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

META-CRESOLSULFONEPHTHALEIN, 3,6-DIMETHYLSULFONEFLUORAN AND SOME OF THEIR DERIVATIVES

BY W. R. ORNDORFF AND A. C. PURDY[1]

RECEIVED MAY 27, 1926 PUBLISHED AUGUST 5, 1926

The condensation of *m*-cresol with the anhydride or chlorides of *o*-sulfobenzoic acid was undertaken to prepare *m*-cresolsulfonephthalein. No mention of this phthalein was found in the literature. While this work was in progress, however, Cohen[2] published a preliminary note in which he mentioned *m*-cresolsulfonephthalein and tetrabromo-*m*-cresolsulfonephthalein. He stated that the former gave a color change from yellow to purple at a *P*H of 7.6–9.2, while the latter changed from yellow to blue-green at a *P*H of 4.0–5.6, but he gave no details as to the method of preparation or properties of these sulfonephthaleins, nor were any analyses given.

Investigations carried out in this Laboratory[3] have shown that the con-

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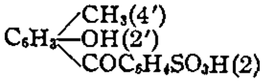
[1] From a dissertation presented by A. C. Purdy to the Faculty of the Graduate School of Cornell University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

We are indebted to the Monsanto Chemical Works, who very kindly furnished gratis the saccharin used in this investigation.

[2] Cohen, "Some New Sulfonephthalein Indicators," *Pub. Health Repts.*, **38**, 199 (1923).

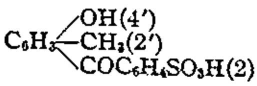
[3] Orndorff and Sherwood, THIS JOURNAL, **45**, 486 (1923). Orndorff and Vose, *ibid.*, **46**, 1896 (1924). Orndorff and Cornwell, *ibid.*, **48**, 981 (1926).

densation of a phenol with the anhydride of *o*-sulfobenzoic acid takes place in two stages, an addition product, the intermediate acid being first formed, which then reacts with a second molecule of the phenol to give the sulfonephthalein. In the case of *m*-cresol there are two such intermediate acids (I and II) theoretically possible.



$C_6H_3\begin{cases}CH_3(4')\\OH(2')\\COC_6H_4SO_3H(2)\end{cases}$

I

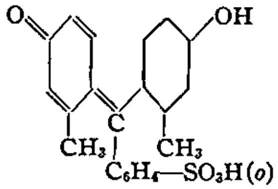


$C_6H_3\begin{cases}OH(4')\\CH_3(2')\\COC_6H_4SO_3H(2)\end{cases}$

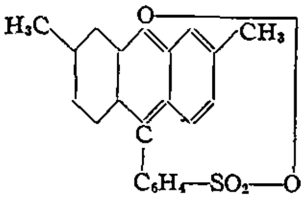
II

I. 2'-Hydroxy-4'-methyl-benzoyl-benzene-2-sulfonic acid.
II. 4'-Hydroxy-2'-methyl-benzoyl-benzene-2-sulfonic acid.

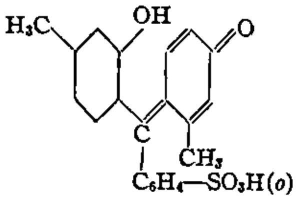
These intermediate acids on condensation with *m*-cresol could form three possible compounds (III, IV and V).



III



IV



V

m-Cresolsulfonephthalein (III), the di-*para* compound in which the hydroxyl groups are *para* to the methane carbon atom, was isolated from the condensations carried on at a temperature of 105–110°. Dimethylsulfonefluoran (IV), the anhydride of the di-*ortho* compound, was obtained from the condensation carried on above 135°. The *ortho-para* compound (V) was not obtained. *m*-Cresolsulfonephthalein (III) was shown to be the di-*para* compound by fusing it with solid sodium hydroxide and isolating 5-hydroxyl-1-methyl-2-benzoic acid from the products of the decomposition. In a like manner the dimethylsulfonefluoran (IV) was shown to be the anhydride of the di-*ortho* compound by identifying 3-hydroxy-1-methyl-4-benzoic acid among the products of its decomposition with alkali.

m-Cresolsulfonephthalein is a highly colored substance, indicating a quinoid structure. Since the crystalline material always contains about 1% of water, it may be considered a solid solution of the inner carbonium or inner oxonium salt and the quinoid hydrate similar to the other sulfonephthaleins[3] studied in this Laboratory. *m*-Cresolsulfonephthalein reacts as a tautomeric substance, and colorless derivatives of the lactoid form and colored derivatives of the quinoid form were made. A colorless modification of *m*-cresolsulfonephthalein was not obtained.

The red *m*-cresolsulfonephthalein dissolves in water with development of a *yellow* color, due to the formation of the carbinol and a small amount of the quinoid hydrate. When this solution is heated it assumes an orange-red color, as some of the carbinol is converted into the quinoid hydrate, which loses water to give the quinoid form of the phthalein. Strong acids also give a red color when added to the *yellow* solution of the phthalein, due to the conversion of some of the carbinol into the quinoid hydrate, which then splits off water to form the quinoid salt with the acid.[4] Alkaline solutions of this sulfonephthalein are purple, due to the formation of highly colored salts with a quinoid structure.

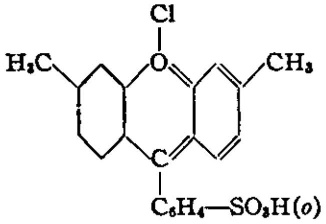
Tetrabromo-*m*-cresolsulfonephthalein was obtained in the *colorless*, lactoid form, but it gives a colored hydrate having the quinoid structure. On being heated, however, this hydrate loses water and leaves the colorless, tetrabromo compound.

Unlike the fluorans previously investigated, 3,6-dimethylsulfonefluoran (IV) is a colored compound. Its color and its neutral character point to its being an inner oxonium or carbonium salt.

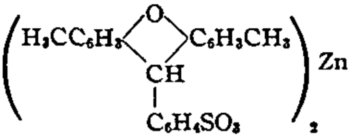
This sulfonefluoran does not absorb ammonia but it combines with one molecule of dry hydrogen chloride, giving a colored hydrochloride (VI) with an *ortho*-quinoid structure.

When this substance is dissolved in concd. sulfuric acid the solution exhibits the fluorescence characteristic of fluorans.

When suspended in water, dimethylsulfonefluoran is reduced by boiling with zinc dust, giving the zinc salt of dimethylhydrosulfofluoranic acid (VII).



VI



VII

This is a very stable salt, showing that its structure no longer resembles that of the sulfonefluoran, which does not form salts.

On bromination of the sulfonefluoran, a dibromodimethylsulfonefluoran was obtained. This also is a highly colored product. The introduction of the bromine atoms increases the acid properties of the sulfonefluoran as the dibromo derivative absorbs ammonia and gives a stable tri-ammonia compound. Because of its color the dibromo compound is also to be represented as an inner oxonium or carbonium salt. The position of the bromine atoms in the molecule was not determined.

Experimental Part

m-Cresol.—The *m*-cresol used was obtained from Kahlbaum and from Eastman. The first sample boiled at 199.3–200.3° (742.3 mm.) and gave a freezing point of 4.75°. The second (*m*-cresol, "practical") boiled at

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[4] See benzaurin, This Journal, 47, 2770 (1925).

199.0–199.8° (737.5 mm.). A quantitative determination of the *m*-cresol in these products by the Barrett modification of the Raschig nitration method gave 90.8% for the former and 98.2% for the latter. The impurity is presumed to be *p*-cresol. Dawson and Mountford's[5] freezing-point curve for mixtures of *m*- and *p*-cresol gave 91.36% of *m*-cresol in the mixture freezing at 4.75°.

Condensation of *m*-Cresol with *o*-Sulfobenzoic Acid Anhydride.—The products of the condensation of *m*-cresol with *o*-sulfobenzoic acid anhydride depend on the temperature.

A. Condensations below 110°.—The anhydride[6] (1 mole) was dissolved in *m*-cresol (2 moles plus a slight excess), and zinc chloride (weight equal to that of the *m*-cresol) was slowly added during stirring. This mixture was heated at 105–108° until the mass solidified. Water was then added and the excess of *m*-cresol removed by steam distillation. The residue was extracted with a hot 10% sodium carbonate solution, the extract filtered, diluted and acidified with dil. hydrochloric acid. On cooling, the sulfonephthalein was obtained as fine, beetle-green crystals. The zinc chloride did not increase the yield but shortened the time necessary for the reaction. Yields of the sulfonephthalein were about 15%.

B. Condensation from 125–145°.—A mixture of *m*-cresol and the anhydride in the proportions given above was heated for 48 hours at 145°, but no condensing agent was employed. The mixture was then thoroughly extracted with hot water. The water solutions were concentrated to crystallization, and the yellow-orange crystalline product was recrystallized from hot water. On analysis this product, which was obtained with a 20% yield, proved to be dimethylsulfonefluoran (IV).

Product Insoluble in 10% Sodium Carbonate.—In all the fusions of *m*-cresol with the anhydride of *o*-sulfobenzoic acid very appreciable quantities of a highly colored substance insoluble in water and 10% sodium carbonate solution were obtained. It contained about 3–4% of sulfur, but the results of the analyses varied and all attempts to prepare the substance itself or any of its derivatives in a pure crystalline condition were unsuccessful.

Reaction of *m*-Cresol with the Chlorides of *o*-Sulfobenzoic Acid.—A modification of the method of Remsen and Dohme[7] was used to prepare the chlorides. *m*-Cresol was condensed with the sulfonechlorides, at a temperature of 105–110°, using zinc chloride as a condensing agent. The proportions used and the treatment of the reaction product were the same as described above in the anhydride condensations below 110°. Yields of 20% of the pure *m*-cresolsulfonephthalein were obtained by this method.

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[5] Dawson and Mountford, *J. Chem. Soc.*, **113**, 923 (1918).

[6] White and Acree, THIS JOURNAL, **41**, 1197 (1919).

[7] Orndorff and Cornwell, *ibid.*, **48**, 981 (1926).

m-Cresolsulfonephthalein.—Air-dried samples of the sulfonephthalein were found to contain about 1% of water.

Anal.[8] Subs., 1.1065, 1.0336: loss at 125°, 0.0110, 0.0103. Found: H_2O, 0.99%, 1.0%.

Subs. (dry), 0.3009, 0.3205, 0.3121, 0.3693: $BaSO_4$, 0.1804, 0.1942, 0.1871, 0.2229. Calcd. for $C_{21}H_{18}SO_5$: S, 8.38. Found: 8.24, 8.32, 8.23, 8.29. (The first two samples analyzed are from the anhydride condensation and the latter two from the chloride condensation.)

Pure *m*-cresolsulfonephthalein crystallizes with a beetle-green surface color. When ground it gives a deep red powder. From cold alkaline solutions it is precipitated in reddish flocks upon the addition of acid. At the boiling temperature the acid precipitates it in a dark colored, amorphous form. In order to precipitate it in a crystalline form it was found advantageous to acidify a hot 5% sodium carbonate solution of such a dilution that the sulfonephthalein comes out gradually on concentration of the slightly acid solution. *m*-Cresolsulfonephthalein is slightly soluble in water, quite soluble in ethanol and methanol, and acetic acid, and insoluble in benzene, ether, chloroform, carbon tetrachloride, ethyl acetate and petroleum ether. Its saturated aqueous solution is orange-red, changing to bright red on the addition of a mineral or strong organic acid. It dissolves in concd. sulfuric acid with development of a deep cherry-red color. *m*-Cresolsulfonephthalein dissolves in solutions of sodium hydroxide, sodium carbonate and bicarbonate, and ammonium hydroxide, giving a highly colored solution which appears purple in thin layers and red in thick layers. On dilution a purple solution is obtained.

With aniline, *m*-cresolsulfonephthalein reacts in the same way as the other sulfonephthaleins.[3] It dissolves with development of a red color, which changes to green when the solution is heated to the boiling point. On cooling and acidifying this solution with hydrochloric acid, a flocculent green precipitate is formed, analogous to the diphenylamine-sulfonephthalein isolated by Sherwood.[3] *m*-Cresolsulfonephthalein is practically insoluble in cold dimethylaniline, but dissolves to a slight extent when heated, giving an amber-colored solution.

m-Cresolsulfonephthalein does not have a definite melting point, but deepens in color when heated and gradually shrivels and carbonizes between 250° and 300°.

The following derivatives of *m*-cresolsulfonephthalein were made.

AMMONIUM SALT.—A sample of pure, dry *m*-cresolsulfonephthalein absorbed about 3 molecular proportions of dry ammonia gas. The resulting product was deep red and was easily soluble in water with development of a deep red color. It lost ammonia on standing in a desiccator over concd. sulfuric acid and gave a stable, lighter red monoammonium salt.

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[8] International atomic weights for 1925 were used in the calculations in this paper, THIS JOURNAL, 47, 600 (1925).

Anal. Subs., 0.2245: gain, 0.0096. Calcd. for $C_{21}H_{18}SO_5$ + 1 NH_3: NH_3, 4.26. Found: 4.10.

Barium Salt.—An excess of barium carbonate was boiled with an aqueous suspension of *m*-cresolsulfonephthalein, until the latter had completely dissolved. The filtered solution was evaporated to dryness, and the resulting dark red product was extracted with ethanol. The salt did not crystallize so the alcoholic extract was evaporated to dryness and the residue ground, dried in the air and analyzed. It proved to be the barium salt of *m*-cresolsulfonephthalein containing two molecules of alcohol, which it lost on drying at 135°.

Anal. Subs., 0.2499, 0.2272: loss at 135°, 0.0238, 0.0214. Calcd. for $C_{42}H_{34}S_2O_{10}$-Ba + 2 C_2H_5OH: C_2H_5OH, 9.28. Found: 9.52, 9.42.

Subs. (after heating at 135°), 0.4323, 0.4547: $BaSO_4$, 0.1112, 0.1166. Calcd. for $C_{42}H_{34}S_2O_{10}Ba$: Ba, 15.27. Found: 15.14, 15.10.

Diacetate.—Four g. of pure *m*-cresolsulfonephthalein was boiled with 50 cc. of acetic anhydride for one- and one-half hours. The diacetate was recrystallized from ether, and obtained as colorless needles melting at 172–173°.

Anal. Subs., 0.3942, 0.3514: $BaSO_4$, 0.1918, 0.1728. Calcd. for $C_{21}H_{16}SO_5$-$(OCCH_3)_2$: S, 6.87. Found: 6.68, 6.75.

The diacetate is readily saponified by cold sodium hydroxide solution, but is not hydrolyzed by boiling water. It is readily soluble in glacial acetic acid and benzene, quite soluble in ether, but insoluble in water and petroleum ether.

Dibenzoate.—Five g. of pure *m*-cresolsulfonephthalein in 20 g. of benzoyl chloride was heated at 140–145° for two hours. The excess of benzoyl chloride was evaporated in a water-oven through which a current of dry air passed. The residue was recrystallized from ether, giving colorless needles; m. p., 208–209°.

Anal. Subs., 0 3784, 0.3933: $BaSO_4$, 0.1441, 0.1518. Calcd. for $C_{21}H_{16}SO_5$-$(OCC_6H_5)_2$: S, 5.42. Found: 5 22, 5.30.

The dibenzoate is soluble in benzene, very slightly soluble in cold ether, and insoluble in petroleum ether and water. It is very stable toward cold sodium hydroxide solution, but is slowly saponified by boiling with this solution.

Dimethyl Ethers. *A. Colorless Form.*—Ten g. of pure, dry *m*-cresolsulfonephthalein was boiled with 500 cc. of methyl alcohol for 50 hours. The solution was then evaporated to dryness and the residue extracted with ether. The dimethyl ether was obtained as colorless crystals, which turned faintly pink when air-dried. It turns red when heated and melts to a dark red liquid at 164–165°.

Anal. Subs., 0.2969, 0 3013: $BaSO_4$, 0.1669, 0.1684. Subs., 0.1692, 0.1728: AgI, 0.1989, 0.2018. Calcd. for $C_{21}H_{16}SO_3(CH_3O)_2$: S, 7.81; OCH_3, 15.13. Found: S, 7.72, 7.66; OCH_3, 15.53, 15.43.

The colorless dimethyl ether of *m*-cresolsulfonephthalein is very soluble in methyl alcohol, forming a bright red solution, and in benzene, quite soluble in ether and ethanol and sparingly soluble in water. It is very soluble in acetone, without development of color, but the solution becomes red on the addition of a drop of water. It is readily hydrolyzed by boiling with dilute acids; in fact, boiling with water slowly brings about hydrolysis. It is, however, quite stable toward solutions of the alkalies. It is not acetylated by boiling with acetic anhydride, nor does it absorb dry ammonia gas.

The highly colored mother liquor from the crystallization of the colorless dimethyl ether was evaporated to dryness and the residue extracted with benzene. A few dark red crystals were obtained which proved to be a monomethyl ether, melting at 176–178°.

Anal. Subs., 0 1173: AgI, 0.0674. Calcd. for $C_{21}H_{17}SO_4(CH_3O)$: OCH_3, 7.83. Found: 7.59.

The fact that it dissolves in dil. ammonium hydroxide and is precipitated by hydrochloric acid without changing its melting point indicates that it is the monomethyl ether rather than the monomethyl ester.

B. Colored Form.—A sample of the pure, dry, colorless dimethyl ether of *m*-cresolsulfonephthalein (in a platinum boat) was heated at 170–172° for 20 minutes in a current of dry carbon dioxide. The dark red liquid solidified on cooling. This solid was ground and exposed to dry ammonia gas. The ether did not change in weight during the heating but gained weight on exposure to the ammonia gas. When placed in a desiccator over sulfuric acid this product formed a stable mono-ammonium salt of the colored dimethyl ether of *m*-cresolsulfonephthalein.

Anal. Subs., 0.2980: gain, 0.0119. Calcd. for $C_{21}H_{16}SO_3(OCH_3)_2 + NH_3$: NH_3, 3.98. Found: 3.84.

Tetrabromo-*m*-cresolsulfonephthalein.—A solution of 15 g. of bromine in 125 cc. of glacial acetic acid was added to 20 g. of pure *m*-cresolsulfonephthalein in 250 cc. of glacial acetic acid. The mixture was stirred mechanically for 24 hours. The precipitate was then filtered off and extracted with benzene. The tetrabromo compound was crystallized from benzene and recrystallized from glacial acetic acid. *Colorless* crystals melting at 218–219° were obtained.

Anal. Subs., 0.4837, 0.4720: $BaSO_4$, 0.1551, 0.1547. Subs., 0.1315, 0.1504: AgBr, 0.1421, 0.1612. Calcd. for $C_{21}H_{14}Br_4SO_5$: S, 4.59; Br, 45.80. Found: S, 4.41, 4.50; Br, 45.99, 45.60.

Tetrabromo-*m*-cresolsulfonephthalein is readily soluble in ethyl acetate, ether and ethanol, fairly soluble in benzene, somewhat soluble in glacial acetic acid and sparingly soluble in water. It is very sensitive to alkalies, tap water being sufficiently alkaline to give the characteristic blue-green color.

HYDRATE.—The brick red, amorphous hydrate of tetrabromo-*m*-cresolsulfonephthalein was precipitated by the acidification of the aqueous solution of the tetrabromo compound. The hydrate was filtered off, air-dried and a portion of it heated in a melting-point tube. It turned from red to orange at about 90°, became colorless at about 190°, and melted sharply at 218–219°.

Anal. Subs., 0.4730, 0.4997: loss at 130–135°, 0.0725, 0.0765. Calcd. for $C_{21}H_{14}Br_4SO_5 + 7\ H_2O$: H_2O, 15.30. Found: 15.33, 15.31.

The hydrate also loses seven molecules of water when allowed to stand in a desiccator over concd. sulfuric acid, but regains this water when placed in a desiccator over water. The substance dried at 130–135° does not gain appreciably in weight when placed in a desiccator over water.

DIACETATE.—The diacetate of the tetrabromo compound was prepared in the same manner as the diacetate of the *m*-cresolsulfonephthalein. It was obtained as colorless needles, melting at 235–236°, by recrystallization from ethyl acetate.

Anal. Subs., 0.5060, 0.5138: $BaSO_4$, 0.1478, 0.1487. Subs., 0.1556, 0.1593: AgBr, 0.1486, 0.1518. Calcd. for $C_{21}H_{12}Br_4SO_5(OCCH_3)_2$: S, 4.10; Br, 40.88. Found: S, 4.01, 3.98: Br, 40.64, 40.55.

The diacetate is quite soluble in benzene, ethyl acetate and glacial acetic acid, sparingly soluble in ether and insoluble in water. It is slowly saponified by cold sodium hydroxide solution; more readily by hot alkali. It is readily saponified by cold alcoholic sodium hydroxide solution, but is stable toward boiling water.

DIBENZOATE.—The dibenzoate of the tetrabromo compound was prepared in the same manner as the dibenzoate of the *m*-cresolsulfonephthalein. It was recrystallized from ether, giving colorless crystals melting at 205–206°.

Anal. Subs., 0.5326, 0.5257: $BaSO_4$, 0.1340, 0.1342. Subs., 0.1440, 0.1567:

AgBr, 0.1181, 0.1291. Calcd. for $C_{21}H_{12}Br_4SO_5(OCC_6H_5)_2$: S, 3.54; Br, 35.28. Found: S, 3.46, 3.50; Br, 34.90, 35.06.

The dibenzoate is readily soluble in benzene and ethyl acetate, quite soluble in ether and ethyl alcohol and insoluble in water. It is unaffected by cold aqueous sodium hydroxide, but is slowly saponified by hot alkali. It is readily saponified by hot alcoholic alkali, but it is not decomposed by boiling water.

AMMONIUM SALT.—A sample of pure tetrabromo-*m*-cresolsulfonephthalein absorbed about four molecular proportions of dry ammonia gas. The resulting product was deep purple with a bronze surface color. When allowed to stand in a desiccator over sulfuric acid this compound lost ammonia and yielded a dark colored, stable ammonium salt.

Anal. Subs., 0.4274: gain, 0.0135. Calcd. for $C_{21}H_{14}Br_4SO_5$ + 1 NH_3: NH_3, 2.38. Calcd. for $C_{21}H_{14}Br_4SO_5$ + 2 NH_3: NH_3, 4.64. Found: 3.06.

3,6-Dimethylsulfonefluoran (IV)

Analyses of the yellow-orange crystalline product obtained from the condensation of *m*-cresol with the anhydride of *o*-sulfobenzoic acid at 125–145°, show it to be a dimethylsulfonefluoran.

Anal. Subs., 0.3761, 0.4228: $BaSO_4$, 0.2363, 0.2686. Subs., 0.1184, 0.1423, 0.1410: CO_2, 0.2990, 0 3600, 0 3586; H_2O, 0.0470, 0.0560, 0.0568. Calcd. for $C_{21}H_{16}SO_4$: C, 69.21; H, 4.43; S, 8.80. Found: C, 68.90, 69.02, 69.38; H, 4.44, 4.41, 4.51; S, 8.63, 8.72.

The sulfonefluoran crystallized in flat, orange-colored plates from water or 50% methanol. It was also obtained in small, yellow-orange needles from water. When ground it gives an orange-yellow powder. It does not possess a definite melting point but chars when heated to 280–290°.

Dimethylsulfonefluoran is slightly soluble in water, readily soluble in methanol and chloroform, difficultly soluble in ethanol and acetone, and insoluble in benzene, ether, ethyl acetate and carbon tetrachloride. Its saturated water solution is amber-colored, and undergoes no change in color when heated or acidified. Concd. hydrochloric acid precipitates the sulfonefluoran from its aqueous solution in red flocks.

Dimethylsulfonefluoran dissolves in cold concd. sulfuric acid with development of an amber color, the solution possessing the characteristic greenish fluorescence of the fluorans. On heating, the solution becomes reddish.

The sulfonefluoran is insoluble in 10% sodium carbonate solution, although the solid particles become greenish. When the solution is filtered and hydrochloric acid is added to the filtrate no precipitate is formed. The sulfonefluoran is soluble, however, in cold 5% sodium hydroxide solution with an intense blue color. Hydrochloric acid precipitates it from this solution in orange-colored flocks.

When heated with aniline, the dimethylsulfonefluoran dissolves with a red color, but the resulting solution does not undergo any change in color on boiling. Boiling with acetic anhydride failed to acetylate it and boiling with zinc or barium carbonate in an attempt to form salts apparently caused decomposition. A sample of the pure dry 3,6-dimethylsulfonefluoran turned greenish when exposed to dry ammonia gas but did not gain appreciably in weight.

HYDROCHLORIDE.—When a sample of pure, dry 3,6-dimethylsulfonefluoran was exposed to the action of dry hydrogen chloride, it rapidly gained in weight and turned a reddish color.

Anal. Subs., 0.2600: gain, 0.0254. Calcd. for $C_{21}H_{16}SO_4$ + 1 HCl: HCl, 9.10. Found: 8.90.

ZINC SALT OF THE REDUCTION PRODUCT OF DIMETHYLSULFONEFLUORAN.—An aqueous suspension of 5 g. of the sulfonefluoran was boiled with an excess of zinc dust. The sulfonefluoran dissolved with development of a reddish color, but the solution became colorless on continued boiling. When the liquid was filtered, concentrated and cooled, fine colorless needles separated. These were filtered off and dried in a vacuum desiccator. A portion of this product was dried to constant weight at 130–135° in a current of dry carbon dioxide and analyzed.

Anal. Subs., 0.1724, 0.1547: CO_2, 0.4006, 0.3614; H_2O, 0.0666, 0.0629. Subs., 0.3120, 0.4014: $ZnSO_4$, 0.0623, 0.0797. Calcd. for $C_{42}H_{34}S_2O_8Zn$: C, 63.35; H, 4.31; Zn, 8.21. Found: C, 63.40, 63.73; H, 4.22, 4.55; Zn, 8.01, 7.97.

The zinc salt of dimethylhydrosulfofluoranic acid is quite soluble in hot water, but difficultly soluble in cold water. It is also quite soluble in ethanol. It is not oxidized when oxygen is passed into a boiling alcoholic solution for several hours, nor is the dry salt oxidized when heated in a water-oven. It is, however, very sensitive to light and turned a deep yellow immediately in direct sunlight. The zinc salt is very stable, and its slight solubility in cold water made it impossible to precipitate the zinc completely as zinc sulfide, nor can the zinc be removed by dilute mineral acids in the cold. When it was heated on a water-bath with dil. sulfuric acid in a stream of carbon dioxide, the resulting product gave no test for zinc and when crystallized from 50% methanol gave dimethylsulfonefluoran.

Dibromo-3,6-dimethylsulfonefluoran.—Four g. of bromine in 25 cc. of glacial acetic acid was slowly added to a solution of 4 g. of pure, dry dimethylsulfonefluoran in 75 cc. of glacial acetic acid during mechanical stirring. After stirring had been continued for 24 hours the crystalline bromine compound was filtered off and air-dried. The air-dried product was orange-red and when ground gave an orange powder. An air-dried sample was dried to constant weight at 125°.

Anal. Subs., 0.2049, 0.2273: loss at 125°, 0.0298, 0.0326. Calcd. for $C_{21}H_{14}Br_2SO_4 + 1.5\ C_2H_4O_2$: $C_2H_4O_2$, 14.71. Found: 14.54, 14.34.

Another portion of the bromine compound after heating at 125° was analyzed and shown to be dibromo-3,6-dimethylsulfonefluoran.

Anal. Subs., 0.2221, 0.2626: $BaSO_4$, 0.1022, 0.1197. Subs., 0.1983, 0.3065: AgBr, 0.1415, 0.2183. Calcd. for $C_{21}H_{14}Br_2SO_4$: S, 6.14; Br, 30.61. Found: S, 6.32, 6.26; Br, 30.37, 30.31.

The dibromo compound is soluble in hot glacial acetic acid, ethanol or methanol and water, slightly soluble in chloroform and insoluble in benzene. When heated it turns dark at about 200°, but does not melt below 300°. In cold, concd. sulfuric acid it gives a yellow solution having a slight, greenish fluorescence.

An attempt to make the tetrabromo compound by bromination in hot glacial acetic acid resulted in dark colored products of varying bromine content, due probably to some of the bromine entering the side chain. There was no evidence of the formation of the oxonium tribromo compound during the bromination in cold glacial acetic acid.

AMMONIUM SALT.—The substitution of two atoms of bromine increases its acid properties so that dibromodimethyl-sulfonefluoran readily absorbs ammonia when placed in dry ammonia gas. When allowed to stand in a desiccator over sulfuric acid this product lost ammonia and yielded a highly colored, stable ammonia compound.

Anal. Subs., 0.1751: gain, 0.0168. Calcd. for $C_{21}H_{14}Br_2SO_4 + 3\ NH_3$: NH_3, 8.66. Found: 8.75.

Summary

1. Pure *m*-cresolsulfonephthalein has been prepared by the condensation of *m*-cresol with the anhydride or chlorides of *o*-sulfobenzoic acid at

105–110°. It is a tautomeric substance, and colored derivatives of the quinoid form (salts) and colorless derivatives of the lactoid form (diacetate, dibenzoate and dimethyl ether) have been made.

2. The colorless dimethyl ether of *m*-cresolsulfonephthalein is converted into a colored quinoid form at 170–172°.

3. Tetrabromo-*m*-cresolsulfonephthalein and its diacetate and dibenzoate have been made. All three are colorless and, therefore have the lactoid structure. Tetrabromo-*m*-cresolsulfonephthalein forms a colored quinoid hydrate and an ammonium salt.

4. Pure 3,6-dimethylsulfonefluoran was prepared by the condensation of *m*-cresol with the anhydride of *o*-sulfobenzoic acid at 125–145°. Unlike the fluorans previously investigated, it is a colored compound and is slightly soluble in water. It is a weak acid and does not form stable salts nor does it absorb dry ammonia gas. With dry hydrogen chloride it gives a colored hydrochloride, analogous to that obtained with 3,6-dimethylfluoran.

5. The colorless zinc salt of the reduction product of 3,6-dimethylsulfonefluoran (3,6-dimethylhydrosulfofluoranic acid) was made.

6. Pure dibromo-3,6-dimethylsulfonefluoran was prepared. It is a colored compound and therefore has the quinoid structure. It absorbs dry ammonia gas and yields a stable ammonia compound due to the introduction of the two bromine atoms.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

3-HYDROXY-TETRACHLOROFLUORAN AND 3,4-DIHYDROXY-TETRACHLOROFLUORAN AND SOME OF THEIR DERIVATIVES

BY W. R. ORNDORFF AND C. H. JOHNSON[1]

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It has been shown in this Laboratory that the formation of the phthaleins from phthalic anhydride and the phenols proceeds in two stages; first, the phenol combines with the anhydride to form the intermediate acid, *p*-hydroxybenzoyl-*o*-benzoic acid in the case of phenol itself, then this acid reacts with another molecule of the phenol to give the phthalein and water. Isophenolphthalein was prepared by Orndorff and Barrett[2] by condensing *o*-hydroxybenzoyl-*o*-benzoic acid with phenol, and Orndorff and Parsons[3] have made isophenol-tetrachlorophthalein from *o*-hydroxybenzoyl-tetra-

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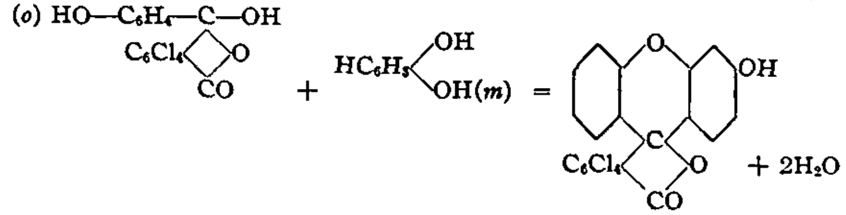
[1] From a dissertation presented to the Faculty of the Graduate School of Cornell University, by C. H. Johnson, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

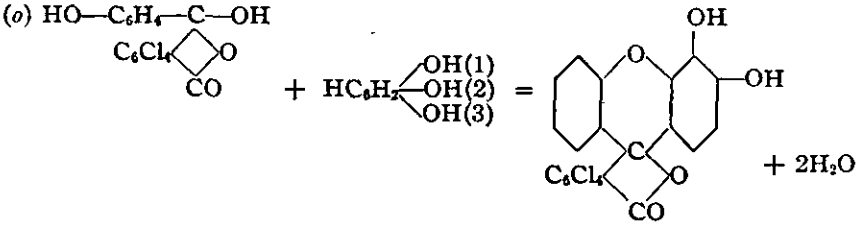
[2] Orndorff and Barrett, THIS JOURNAL, 46, 2483 (1924).

[3] Orndorff and Parsons, *ibid.*, 48, 283 (1926).

chloro-*o*-benzoic acid and phenol. It was thought that *o*-hydroxybenzoyltetrachloro-*o*-benzoic acid would condense with resorcinol and with pyrogallol to give *unsymmetrical* phthaleins containing a pyrone ring.



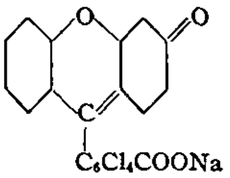
3-Hydroxy-tetrachlorofluoran



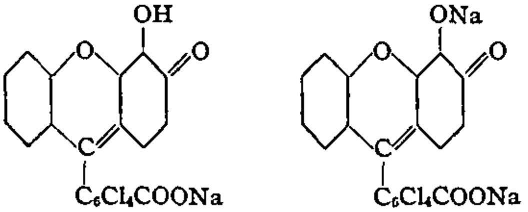
3,4-Dihydroxy-tetrachlorofluoran

As these *unsymmetrical* phthaleins had never been made and it was desirable to investigate them and study their absorption spectra, the present investigation was undertaken.

Both of these compounds have now been made by the method described above, and as they are *colorless* they both have the *lactoid* formulas given above. Their salts are colored, however, and have *quinoid* structures.



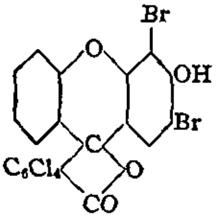
Sodium salt of
3-hydroxy-tetrachloro-
fluoran (colored)



Sodium salts of 3,4-dihydroxy-tetrachloro-
fluoran (colored)

The 3-hydroxy-tetrachlorofluoran gives a mono-acetate and a monobenzoate both of which are colorless and have the lactoid structure. The formation of these substances shows the presence of one hydroxyl group in the lactoid form of the phthalein. The 3,4-dihydroxy-tetrachlorofluoran gives a *colorless* diacetate and dibenzoate as well as a *colorless* monobenzoate, all of which have the *lactoid* structure. The formation of the diacetate and the dibenzoate shows the presence of two hydroxyl groups in the lactoid form of the phthalein. It will thus be seen that the *unsymmetrical* phthaleins, like the symmetrical, act as tautomeric substances.

2,4-Dibromo-3-hydroxy-tetrachlorofluoran is colorless, and has the lactoid structure. It yields a colorless mono-acetate, but forms colored salts. 3,4-Dihydroxy-tetrachlorofluoran gives a monobromo derivative which is colorless and forms a colorless diacetate, but its salts are colored. These bromine derivatives of the unsymmetrical phthaleins also act as tautomeric substances and probably have the following structures.



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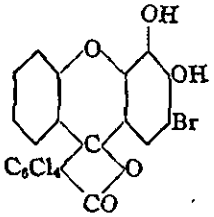
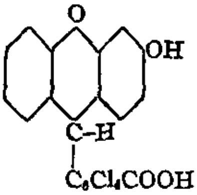


2,4-Dibromo-3-hydroxy-tetrachlorofluoran

2-Bromo-3,4-dihydroxy-tetrachlorofluoran

Like the symmetrical phthaleins, these *unsymmetrical* compounds readily undergo reduction to compounds corresponding to the phthal*ins*. 3-Hydroxy-tetrachloro-hydrofluoranic acid, formed by the reduction of the corresponding fluoran, is analogous to hydrofluoranic acid formed by the reduction of fluoran, and has the following structure as it is colorless and dissolves in alkalies without color.



3-Hydroxy-tetrachloro-hydrofluoranic acid

It yields a colorless mono-acetate which is soluble in alkalies. It is interesting to note that neither of these *unsymmetrical* phthaleins exhibits fluorescence in alkaline solution.

Experimental Part

Preparation of *o*-Hydroxy-benzoyltetrachloro-*o*-benzoic Acid.—This acid was prepared following the directions of Orndorff and Parsons.[3] Analyses and melting-point determinations proved it to be very nearly pure, and it was, therefore, used directly in the work that follows.

3-Hydroxy-tetrachlorofluoran

Preparation.—This compound was prepared from resorcinol and the *o*-hydroxy acid mentioned above. Attempts to prepare it by heating them together, both with and without a condensing agent, at temperatures ranging from 130° to 220° were not successful, since the main product was tetrachloro-fluorescein.[4] Moreover it was very difficult to extract the last traces of tetrachloro-fluorescein from the hydroxy-tetrachlorofluoran, although the former is much more soluble in dilute aqueous alkalies than

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[4] Orndorff and Hitch, This Journal, 36, 680 (1914).

the latter. The formation of tetrachloro-fluorescein is due to the thermal decomposition of the *o*-hydroxy acid and also to condensation of resorcinol with the tetrachloro-phthalic anhydride thus liberated. At the higher temperatures a sublimate of this anhydride on the cooler portions of the flask and air condenser gave additional evidence of the decomposition of the *o*-hydroxy acid by heat.

A method was finally worked out which insured a homogeneous mixture of the reacting substances with the condensing agent at comparatively low temperatures. No tetrachloro-fluorescein is formed by this method, provided the temperature is kept below 130°.

Fifty g. of the *o*-hydroxybenzoyl-tetrachloro-*o*-benzoic acid and 30 g. of resorcinol were ground together and the mixture was added to 150 cc. of acetylene tetrachloride. To this was added 35 g. of fuming stannic chloride. A reddish color developed immediately. The mixture was heated at 120° to 125° for about 24 hours, and the flask shaken frequently during the first hour to dissolve the reagents. As the reaction proceeded, the color of the solution deepened to a very dark red, and the hydroxy-tetrachloro-fluoran settled to the bottom in the form of a reddish-brown tar. At the end of the heating period both the liquid and the tar were transferred to a flask with the aid of steam or hot water. The solvent and the excess of resorcinol were removed by steam distillation, leaving the hydroxy-tetrachlorofluoran as a partially crystalline, orange-yellow solid. This was dried, first at room temperature and then at 120°. The finely divided, orange-yellow powder weighed 60 g. It was completely soluble in a large volume of 1% sodium hydroxide solution. This was poured slowly into an excess of dil. hydrochloric acid, during mechanical stirring. This treatment gave a flocculent, orange-yellow precipitate which was finally dried at 120° and extracted several times with boiling benzene. The combined extracts were boiled with bone black, filtered and about two-thirds of the solvent distilled. From the yellow solution a crop of colorless crystals separated after several hours. Those isolated had a definite crystal form, being short thick needles similar to the crystals of tetrachlorofluoran itself. Subsequent distillations of the solvent gave more colorless crystals until the volume became quite small and impurities gave the solution a red color. The yield was 45 g., or about 75% of that calculated. In later work the alkali treatment was omitted, since the colorless crystals are as readily obtained by extracting the crude product with benzene. A portion of the colorless crystals was recrystallized from benzene, dried to constant weight at 150° and analyzed.

Anal. Subs., 0.1539, 0.1514: cc. of 0.1 *N* $AgNO_3$, 13.5, 13.3. Calcd. for $C_{20}H_8O_4Cl_4$: Cl, 31.25. Found: 31.11, 31.15.

Properties.—The colorless, crystalline product dissolves in dilute aqueous alkalies with development of an orange-red color. It shows no visible fluorescence. It dissolves in concd. sulfuric acid also forming an orange-red solution, and is precipitated therefrom by water. It is slightly soluble in carbon disulfide, ether and petroleum ether, and in glacial acetic acid; soluble in ethanol and methanol with development of a yellow color if a trace of water is present; in chloroform, ethyl acetate and acetone; and in benzene, which is the best solvent for it. The compound is colorless in dilute acid solution, and remains so up to and including *P*H 5.6. It is distinctly yellow at *P*H 6.0. The compound does not melt when heated to 300°. It has the lactoid structure in the solid form and in the acetate and benzoate, but forms colored salts having the quinoid form.

MONO-ACETATE.—Five g. of the hydroxy-tetrachlorofluoran was boiled with 30 cc. of acetic anhydride and 3 g. of fused sodium acetate. The crude, yellow product was purified by crystallization from aqueous acetone, after being decolorized with bone black. The colorless flakes thus secured melted at 198–200°. The acetate is slowly hydrolyzed by dilute aqueous alkalies and by concd. sulfuric acid, giving to the solutions the same orange-red color as the hydroxy-tetrachlorofluoran. It is soluble in acetone, benzene, ethanol and methanol, and in ether. The flakes from acetone were prepared for analysis by drying to constant weight at 150°.

Anal. Subs., 0.1547, 0.1713: cc. of 0.1 *N* $AgNO_3$, 12.5, 13.75. Calcd. for $C_{20}H_7O_4Cl_4(COCH_3)$: Cl, 28.6. Found: 28.65, 28.46.

MONOBENZOATE.—Five g. of the hydroxy-tetrachlorofluoran was boiled with 50 cc. of benzoyl chloride. When the cooled solution was poured into an equal volume of absolute alcohol a colorless, granular substance settled out which, after being washed with alcohol and dried at room temperature, melted at 248–249°. Like the acetate it is hydrolyzed by alkalies and by concd. sulfuric acid, but more slowly. It is soluble in benzene, acetone, ether and ethanol. The air-dried material was heated to constant weight at 160°.

Anal. Subs., 0.1752, 0.1536: cc. of 0.1 *N* $AgNO_3$, 12.5, 11.0. Calcd. for $C_{20}H_7O_4Cl_4(COC_6H_5)$: Cl, 25.42. Found: 25.30, 25.39.

MONO-AMMONIUM SALT.—In an attempt to make the imide[2] by the action of concd. ammonia solution on the hydroxy-tetrachlorofluoran, the ammonium salt, in the form by glistening, red-brown flakes, was obtained. After recrystallization from ethanol and drying, it melted at 277–280° with decomposition. It is soluble in ethanol, methanol, benzene and acetone.

Anal. Subs., 0.1588, 0.1548: cc. of 0.1 *N* $AgNO_3$, 13.6, 13.2. Calcd. for $C_{20}H_7O_4Cl_4NH_4$: Cl, 30.12. Found: 30.37, 30.24.

MONOSODIUM SALT.—Five g. of the 3-hydroxy-tetrachlorofluoran was suspended in about half a liter of ethanol and an excess of freshly prepared sodium ethylate solution added. After boiling for about three hours, half the solvent had distilled and the orange-red salt gradually crystallized. After recrystallization from ethanol, the air-dried substance did not melt when heated to 300°. It lost little weight when heated at 140°.

Anal. Subs., 0.1803, 0.1931: cc. of 0.1 *N* $AgNO_3$, 15.3; Na_2SO_4, 0.0287. Calcd. for $C_{20}H_7O_4Cl_4Na$: Cl, 29.80; Na, 4.83. Found: Cl, 30.09; Na, 4.81.

BARIUM SALT.—Three g. of the crude sodium salt was dissolved in a large volume of very dilute ammonia solution. To the filtered solution was added a slight excess of dil. barium chloride solution. The crude barium salt which precipitated immediately was dried and recrystallized from a mixture of benzene and methanol. The well-formed, orange-red crystals contain about three molecules of water. They are slightly soluble in water and soluble in ethanol, methanol and benzene. The dry substance decomposes when heated slightly above 300°.

Anal. Subs., 0.2364: loss at 165°, 0.0211. Calcd. for $(C_{20}H_7O_4Cl_4)_2Ba + 3H_2O$: H_2O, 9.39. Found: 8.76.

Subs. (dry), 0.1888, 0.1667: $BaSO_4$, 0.0418, 0.0376. Calcd. for $(C_{20}H_7O_4Cl_4)_2Ba$: Ba, 13.17. Found: 13.03, 13.27.

2,4-Dibromo-3-hydroxy-tetrachlorofluoran.—Ten g. of the hydroxy-tetrachlorofluoran was suspended in 150 cc. of glacial acetic acid, and a slight excess of bromine over that calculated for the formation of a tetrabromo derivative was dissolved in a little of the same solvent and added slowly during stirring. After standing for 12 hours and heating on the steam-bath for two hours there was still considerable bromine left. The cream-colored precipitate was filtered off and washed with 80% acetic acid and with water. The color was removed by recrystallization from benzene. The pure substance does not melt when heated to 300°, nor does it lose appreciable weight when heated at 160°.

Anal. Subs., 0.1041, 0.1235: AgCl + AgBr, 0.1597, 0.1892: cc. of 0.1 *N* $AgNO_3$, 10.1, 11.95. Calcd. for $C_{20}H_6O_4Cl_4Br_2$: Cl, 23.18; Br, 26.12. Found: Cl, 22.98, 22.70; Br, 25.73, 26.02.

The dibromo derivative dissolves in concd. sulfuric acid with development of an orange color. It is less soluble in dilute alkalies than the hydroxy-tetrachlorofluoran, and no sodium salt is formed when it is boiled with a slight excess of sodium ethylate solution. The compound dissolves readily in benzene and acetone; it is less soluble in ethanol and glacial acetic acid, and insoluble in water.

MONO-ACETATE.—Three g. of the dibromo-hydroxy-tetrachlorofluoran was boiled with 1 g. of fused sodium acetate and 20 cc. of acetic anhydride. To remove the color the dried compound was dissolved in benzene and boiled with a little bone black. Crystals were secured by boiling off most of the benzene and adding methanol. They retained slightly more than a molecule of benzene, and melted at 290–292°, giving a red liquid.

Anal. Subs., 0.8528: loss at 140°, 0.0997. Calcd. for $C_{20}H_5O_4Cl_4Br_2(COCH_3) + C_6H_6$: C_6H_6, 10.67. Found: 11.69.

Subs. (heated to 140°), 0.1533, 0.1220; AgCl + AgBr, 0.2208, 0.1757: cc. of 0.1 *N* $AgNO_3$, 14.0, 11.2. Calcd. for $C_{20}H_5O_4Cl_4Br_2(COCH_3)$: Cl, 21.70; Br, 24.45. Found: Cl, 22.06, 22.10; Br, 23.50, 23.23.

The mono-acetate is slowly hydrolyzed by dilute alkalies and quickly by concd. sulfuric acid. It is very soluble in acetone and in benzene, and dissolves in glacial acetic acid, ether and ethanol.

Reduction of 3-Hydroxy-tetrachlorofluoran.—Five g. of the hydroxy-tetrachlorofluoran and an equal weight of zinc dust were suspended in about half a liter of glacial acetic acid and the mixture was boiled for five hours. At the end of this time a test portion, made alkaline with sodium hydroxide, failed to give a red color, which indicated that reduction was complete. The reduction product was precipitated with boiled water, working as much as possible in an atmosphere of carbon dioxide. The dried material was crystallized from benzene; m. p., 257–258°. It is soluble in dilute alkalies with development of only a slight yellow color but soon oxidizes to the original hydroxy-tetrachlorofluoran which then gives the red color. The reduction product is much more soluble in ether than the hydroxy-tetrachloro-fluoran, and dissolves readily in acetone, benzene and ethanol. The crystals from benzene were prepared for analysis by heating in a current of carbon dioxide at 140°.

Anal. Subs., 0.1462, 0.1398: cc. of 0.1 *N* $AgNO_3$, 12.8, 12.2. Calcd. for $C_{20}H_{10}O_4Cl_4$: Cl, 31.11. Found: 31.04, 30.94.

The reduction product described above is a derivative of hydrofluoranic acid.[5] It is therefore called 3-hydroxy-tetrachloro-hydrofluoranic acid.

Mono-acetate of 3-Hydroxy-tetrachloro-hydrofluoranic Acid.—Three g. of the freshly prepared acid was converted into the acetate by boiling with sodium acetate and acetic anhydride. It was purified by crystallization from benzene; m. p. (dry), 187–188°.

Anal. Subs., 0.1602, 0.1709: cc. of 0.1 *N* $AgNO_3$, 12.8, 13.7. Calcd. for $C_{20}H_9O_4Cl_4(COCH_3)$: Cl, 28.48. Found: 28.33, 28.42.

The mono-acetate is soluble in benzene, acetone, ethanol and ether. It dissolves very slowly in aqueous alkalies with a pale yellow color which changes to orange-red on long standing, due to oxidation.

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[5] Meyer and Hoffmeyer, *Ber.*, 25, 2118 (1892).

3,4-Dihydroxy-tetrachlorofluoran

Preparation.—This compound was prepared by the method used for the monohydroxy-tetrachlorofluoran, substituting 35 g. of pyrogallol for the resorcinol and increasing the solvent to about 200 cc. During the condensation the color of the mixture became successively red, violet-red and finally a dark brown. The dihydroxy-tetrachlorofluoran separated in the form of a black tar. It was worked up in the same manner as the monohydroxy compound and weighed 92 g. The crude material was extracted with about 5 liters of boiling benzene, from which it was obtained in the form of reddish-brown or gray-green, thick needles, the color depending on the concentration of the solution. It seems probable that the pure compound is colorless since the colors and shades vary with successive crystallizations, and since it was possible to obtain crystals possessing only a very pale tint of the above colors. Samples were heated to constant weight at 160°.

Anal. Subs., 0.1551, 0.1525, 0.1818: cc. of 0.1 *N* $AgNO_3$, 13.1, 12.9, 15.3. Calcd. for $C_{20}H_8O_5Cl_4$: Cl, 30.19. Found: 29.95, 29.98, 29.84.

The benzene-soluble material amounted to 41 g.; yield, about 65%. There remained of the crude material about 52 g. of grayish-black powder only slightly soluble in this solvent. Efforts to crystallize it from various solvents failed. It gives a dirty brown precipitate with dilute alkalies, and probably is partially oxidized pyrogallol together with stannic acid. If the condensation is carried out at lower temperatures, and especially if for shorter times (up to 12 hours) this material is obtained in large quantity.

Properties.—This compound dissolves in dilute aqueous alkalies with development of a very deep blue color, and is precipitated therefrom as a flocculent brown precipitate on the addition of dilute acids. It dissolves in concd. sulfuric acid forming a deep red solution and is reprecipitated by water. It has about the same solubilities as the monohydroxy-tetrachlorofluoran, and gives a *pink* color to ethanol and to methanol if these solvents contain a little moisture. In dilute acid solutions the compound is colorless and remains so up to and including *P*H 4.8. From *P*H 5.2 to 8.8 inclusive the color is pink. At *P*H 9 2 it becomes distinctly blue. It does not melt when heated to 300°. 3,4-Dihydroxy-tetrachlorofluoran is isomeric with tetrachloro-fluorescein, but it shows no visible fluorescence in alkaline solution. It resembles tetrachlorogallein more closely in its behavior. The blue alkaline solution very slowly becomes pink and then pale yellow due to oxidation.

DIACETATE.—Seven g. of the dihydroxy-tetrachlorofluoran was boiled with 40 cc. of acetic anhydride and 4 g. of fused sodium acetate. The crude yellow-gray substance was dried and purified by repeated crystallization from aqueous acetone, after it had been decolorized with bone black. The small flakes thus secured retain a slight grayish tint; m. p., 215–220°, with some decomposition. The diacetate is slowly hydrolyzed by dilute alkalies and by concd. sulfuric acid. It is soluble in acetone, benzene, ether, and in ethanol and methanol. The flakes from acetone lost no appreciable weight when heated at 150°.

Anal. Subs., 0.1660, 0.1817: cc. of 0.1 *N* $AgNO_3$, 11.9, 13.0. Calcd. for $C_{20}H_6O_5Cl_4(COCH_3)_2$: Cl, 25 61. Found: 25.42, 25.37.

DIBENZOATE.—Five g. of the dihydroxy-tetrachlorofluoran was boiled with 50 cc. of benzoyl chloride. The excess of benzoyl chloride was removed by heating the flask on a steam-bath while passing a current of air into it. The dark brown solid resulting from this treatment was dissolved in benzene and decolorized with bone black. It was obtained in crystalline form by adding ethanol and distilling part of the mixed solvent. The colorless crystals were well formed and contained one-half a molecule of benzene after being air dried at room temperature; m. p., 140°, again at 220°. Like the acetate it is hydrolyzed by alkalies and by concd. sulfuric acid, but more slowly. It dissolves very readily in the usual organic solvents, even at room temperature.

Anal. Subs., 0.1894, 0.1933: loss at 150°, 0.0098, 0.0102. Calcd. for $C_{20}H_6O_5Cl_4(COC_6H_5)_2 + 0.5C_6H_6$: C_6H_6, 5.44. Found: 5.17, 5.28.

Subs. (heated to 150°), 0.1796, 0.1831: cc. of 0.1 *N* $AgNO_3$, 10.5, 10.8. Calcd. for $C_{20}H_6O_5Cl_4(COC_6H_5)_2$: Cl, 20.93. Found: 20.73, 20.92.

Monobenzoate.—Three g. of the dihydroxy-tetrachlorofluoran was dissolved in about 35 cc. of 1% sodium hydroxide solution and 3.5 cc. of benzoyl chloride was added slowly during vigorous shaking. After half an hour the gray-brown precipitate was filtered off and washed with a large volume of water. The dried material was extracted with benzene, and after it had been decolorized with bone black, colorless crystals were obtained by distilling part of the solvent and allowing the solution to cool; m. p. (air-dried), 238–240°. They are somewhat more readily hydrolyzed than the dibenzoate and are readily soluble in the usual organic solvents. A portion was dried to constant weight at 160°.

Anal. Subs., 0.1435, 0.1702: cc. of 0.1 *N* $AgNO_3$, 9.9, 11.8. Calcd. for $C_{20}H_7O_5Cl_4(COC_6H_5)$: Cl, 24.72. Found: 24.46, 24.59.

It is of interest to note that tetrachloro-fluorescein[4] forms a monobenzoate by the Baumann-Schotten reaction and a dibenzoate when boiled with benzoyl chloride.

Monosodium Salt.—Five g. of the dihydroxy-tetrachlorofluoran was suspended in a liter of 95% ethanol and boiled with 2.5 g. of sodium acetate for about five hours. The crude product was obtained by distilling part of the solvent and cooling the solution. It was recrystallized from ethanol, dried to constant weight at 150° and analyzed.

Anal. Subs., 0.1571, 0.2316: Na_2SO_4, 0.0232, 0.0337. Calcd. for $C_{20}H_7O_5Cl_4Na$: Na, 4.68. Found: 4.78, 4.71.

The monosodium salt is only slightly soluble in water, but the presence of a little alkali or ammonia in the water causes it to dissolve with development of a blue color. The recrystallized product is brown and is not well crystallized. It does not melt when heated to 300°.

Disodium Salt.—Ten g. of the dihydroxy-tetrachlorofluoran was treated with 2 g. of sodium in ethanol in the same manner that was described for the monohydroxy-tetrachlorofluoran. The product that crystallizes from ethanol is grayish-brown. It loses very little weight when heated at 140° and does not melt when heated to 300°. It dissolves in the same solvents as the monosodium salt and gives the same blue color in dilute alkalies and ammonia solutions.

Anal. Subs., 0.2572, 0.1974: Na_2SO_4, 0.0701, 0.0541. Calcd. for $C_{20}H_6O_5Cl_4Na_2$: Na, 8.95. Found: 8.82, 8.87.

Monobromo Derivative.—Ten g. of the dihydroxy-tetrachlorofluoran was suspended in 150 cc. of glacial acetic acid and a slight excess of bromine over that calculated for the formation of a tribromo derivative was added. The compound was worked up in much the same manner as was 2,4-dibromo-3-hydroxy-tetrachlorofluoran. The crystals from benzene lost little weight when heated in carbon dioxide at 150°, nor did they melt when heated to 300°.

Anal. Subs., 0.1165, 0.1285: AgCl + AgBr, 0.1594, 0.1760: cc. of 0.1 *N* $AgNO_3$, 10.5, 11.55. Calcd. for $C_{20}H_7O_5Cl_4Br$: Cl, 25.84; Br, 14.55. Found: Cl, 25.82, 25.40; Br, 13.7, 14.43.

If the acetic acid filtrate from the crude monobromo derivative is poured into water, a grayish precipitate is secured which contains only a small percentage of bromine. It is probably an oxidation product of the dihydroxy-tetrachlorofluoran, since it alone results when a large excess of bromine is used during the bromination. The monobromo derivative dissolves in concd. sulfuric acid with development of a red color, and in dilute alkalies with formation of a deep blue color. It remains colorless up to and including a *P*H value of 3.2. From *P*H 3.6 to 8.4 it is pink, and the blue color develops at *P*H 8.8. The compound is soluble in benzene, acetone and ethanol; slightly soluble in glacial acetic acid, and insoluble in water.

Diacetate of 2-Bromo-3,4-dihydroxy-tetrachlorofluoran.—Three g. of the monobromo derivative was converted to the acetate in the usual way. The crude material was dissolved in benzene, decolorized with bone black and allowed to crystallize from this solvent. The crystals hold one-half a molecule of benzene; m. p., 268–270°, with some decomposition.

Anal. Subs., 0.3738: loss at 140°, 0.0235. Calcd. for $C_{20}H_5O_5Cl_4Br(COCH_3)_2$ + 0.5 C_6H_6: C_6H_6, 5.81. Found: 6.29.

Subs. (heated at 140°), 0.1316, 0.1172: AgCl + AgBr, 0.1574, 0.1401; cc. of 0.1 *N* $AgNO_3$, 10.4, 9.25. Calcd. for $C_{20}H_5O_5Cl_4Br(COCH_3)_2$: Cl, 22.41; Br, 12.63. Found: Cl, 22.75, 23.0; Br, 11.75, 11.55.

The diacetate is quite slowly hydrolyzed by dilute aqueous alkalies and by concd. sulfuric acid. It is very soluble in acetone and benzene, and dissolves also in ethanol, glacial acetic acid and ether.

Action of Dry Ammonia Gas on the Hydroxy-tetrachlorofluorans and their Bromo Derivatives.—Small samples of the four compounds were placed in porcelain boats and heated to constant weight at 130°. The samples were then transferred to a combustion tube through which a slow current of dry ammonia gas was being passed. The ammonia was dried first by soda lime and then by sodium wire. The results are given in Table I.

TABLE I

ABSORPTION OF DRY AMMONIA

	Subs., g.	NH_3 absorbed	NH_3, %	Mols of NH_3	Color
$C_{20}H_8O_4Cl_4$	0.2368	0.0009	0.38	0	Yellow
$C_{20}H_6O_4Cl_4Br_2$	.5278	.0150	2.76	1	Orange-yellow
$C_{20}H_8O_5Cl_4$	.2000	.0089	4.26	1.22	Dark brown
$C_{20}H_7O_5Cl_4Br$	.4842	.0410	7.80	2.74	Blue-black

In each case the color appeared immediately upon admitting the ammonia gas, but the gain in weight was slow, the samples taking from six to eight hours to reach constant weight. The absorbed ammonia is readily lost when the samples are heated in a current of dry air at 130° and the original weights of almost colorless compounds are secured. The relatively greater absorption of ammonia gas in the bromo derivatives demonstrates the acidifying influence of the bromine atoms.

Summary

1. *3-Hydroxy-tetrachlorofluoran*, and *3,4-dihydroxy-tetrachlorofluoran* have been prepared from the "intermediate acid" (*o*-hydroxybenzoyl-tetrachloro-*o*-benzoic acid) and resorcinol and pyrogallol, respectively. Like the symmetrical phthaleins, they are tautomeric.

2. These hydroxy-tetrachlorofluorans are colorless as are also their

acetates and benzoates. These *colorless* compounds are therefore given the *lactoid* structure.

3. These hydroxy-tetrachlorofluorans, however, form *colored* sodium, ammonium and barium salts which are given the *quinoid* structure.

4. *2,4-Dibromo-3-hydroxy-tetrachlorofluoran,* and *2-bromo-3,4-dihydroxy-tetrachlorofluoran* have been prepared from the corresponding hydroxy-tetrachlorofluorans. They are *colorless* and form *colorless* acetates. However, they also are tautomeric, since they absorb ammonia gas and dissolve in alkalies with the development of color.

5. *3-Hydroxy-tetrachloro-hydrofluoranic acid* has been prepared by the reduction of the corresponding hydroxytetrachloro-fluoran. This acid and its acetate are *colorless* and dissolve in alkalies without development of color.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE FIRESTONE TIRE AND RUBBER COMPANY]

AN IMPROVEMENT IN MACMULLIN'S AUTOMATIC APPARATUS FOR DETERMINING THE MELTING POINTS OF ORGANIC COMPOUNDS

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In studying MacMullin's description and operation of an automatic melting-point apparatus[1] it was concluded that any errors arising from lag in temperature could be eliminated by employing an automatic device that would remove the maximum thermometer from the bath at the instant the substance melted, and thereby improve the accuracy of the apparatus and decrease the time required for a determination.

With this idea in mind the MacMullin apparatus was modified in such a way that when the substance melted and shut off the heating circuit, it also started a motor which removed the thermometer from the bath. When the thermometer was withdrawn the motor was automatically shut off, thereby raising the thermometer to a definite height and eliminating any possibility of breaking it.

Apparatus.—Referring to Fig. 1, A represents the maximum thermometer, B the mercury bath, C the pulley over which the cord supporting the thermometer passes, D the point of attachment of the thermometer cord on Disk F (diameter = 10 cm.), E the point of attachment of the switch cord on Disk G (diameter = 5.6 cm.), H the motor (an ordinary fan motor, J the throw arm of the single-pole single-throw switch K, L the relay, M the 110-volt power line and N the connections to the coil posts of the relay of the MacMullin apparatus. The disks may be made of Beaver Board,

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[1] MacMullin, THIS JOURNAL, 48, 439 (1926).

G being on the side toward the motor. The cord from E to J is firmly attached on the circumference of G. D is an idler, so that if the motor should continue to run, the thermometer is merely raised and lowered. The thermometer is guided by passage through holes in two corks.

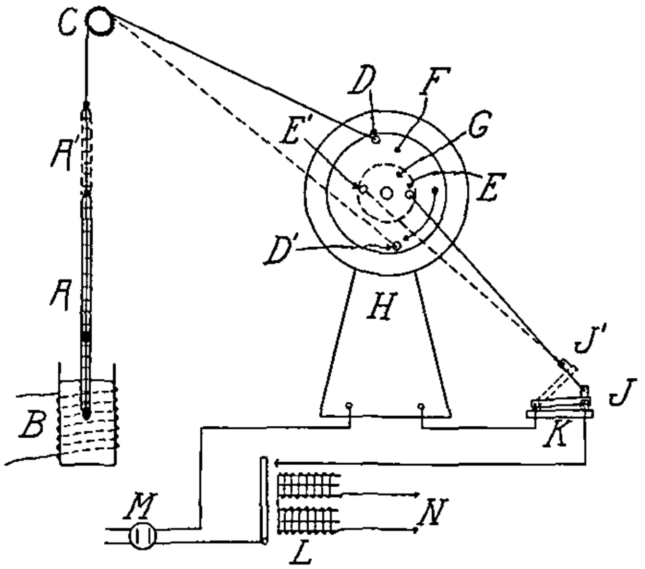

Fig. 1.

Method of Operation.—When the compound melts, contact is made through the relay L, thereby starting the motor which turns in the direction of the arrow. After the motor has made about a quarter revolu-

TABLE I

COMPARISON OF MELTING POINTS (°C.)

	MacMullin app.	Deviation from av.	Improved app.	Deviation from av.	Capillary tube	Inter. Crit Tables (*Vol I*)
p-Dichlorobenzene	55.3	+1.0	53.2	0	53.2	52.9
	54.5	+0.2	53.2	0	53.2	
	53.8	− .5	53.2	0		
	53.5	− .8	53.2	0		
Av.	54.3		53.2		53.2	
Acetanilide	115.3	−0.3	114.8	−0 3	115	114 2
	116.1	+ .5	115.3	+ .2	115	
	116.0	+ .4	114.9	− 2		
	115.0	− .6	115.1	0		
	114.9	− .7	115.1	0		
	116.1	+ .5	115.1	0		
Av.	115.6		115.1		115	
Salicylic acid	161.0	+1.2	159.0	+0.1	159.4	159
	159.6	−0.2	158.6	− .3	159.2	
	158.8	−1.0	159.0	+ .1	159.3	
Av.	159.8		158.9		159.3	

tion the cord from E to J opens the switch, thereby breaking the contact in the power line, and the pull on the switch tends to act as a brake to stop the motor in the position indicated by the primed letters. D has thereby moved to D′ and in so doing has withdrawn the thermometer to a position about 5 cm. above the surface of the bath. It was found by several trials that the maximum point registered on the thermometer was not altered by this method of removal from the bath. The table shows the relationship between melting points obtained with the MacMullin apparatus and with the improved apparatus. The temperatures given are all corrected and the same thermometer was used in all cases.

From Table I it is readily seen that the results obtained with the improved apparatus are by far the more consistent and are nearer to the correct readings as determined by the capillary-tube method.

Different rates of heating produce different temperature lags in the MacMullin apparatus, whereas the results obtained by the improved method are practically independent of the rate of heating. One example will suffice to show these differences.

Wattage	Temp. rise °C. per min.	Melting points (°C.) MacMullin app.	Melting points (°C.) Improved app.
115	1.5	122.7	122.4
175	8	123.8	122.7

Calibration of the apparatus for radiation and rate of heating is therefore unnecessary and less time is consumed for each determination, an item which is of particular interest to one who has several melting points to determine.

Summary

An improvement in an automatic melting point apparatus for organic compounds has been described.

It has been shown that the precision obtained with this improvement is comparable to that obtained by the capillary tube method.

It has also been shown that the results obtained are practically independent of the rate of heating and that calibration of the apparatus is therefore unnecessary.

AKRON, OHIO

[Contribution from the Chemical Laboratory of the University of Saskatchewan]

ACTION OF ANILINE ON GLUCOSE IN ACETIC ACID SOLUTION. I

By C. N. Cameron

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In the past considerable work[1] has been done on the action of bases on sugars under various conditions, the effect, briefly, being one of preliminary enolization followed by dissociation of the sugar molecule. The action of acids on the hexoses,[2] leading to the production of hydroxymethyl-furfural, levulinic acid, formic acid and humus, has been investigated. Further, it has been found that amino acids act on carbohydrates[3] with the loss of carbon dioxide and formation of dark brown condensation products. However, the simultaneous effect of a weak base (aniline) and a weak acid (acetic) on glucose has not been recorded.

The more obvious effect produced when primary aromatic amines, such as aniline, and acetic acid are added to alcoholic solutions of glucose is the final appearance of a brown coloration, even at room temperature. This coloration is more rapid in such acid solutions than with glucose and aniline alone, glucose and acetic acid, aniline and acetic acid or aniline alone in alcohol. When water is used as the solvent, the colored material precipitates. It is believed that the initial step is the formation of a compound between the amine and the glucose and that this reaction is catalyzed by the acid. That the compound, glucose-anilide, is produced in acid solutions of glucose and aniline and that this reaction is more rapid in the presence of acid is shown below. That the coloration is due primarily to the formation of the compound, glucose-anilide, is indicated by the fact that this substance in acid solution gives apparently the same colored material.

The further changes, it is hoped, will be dealt with later although it might be mentioned that the color seems to be due in part to the oxidation of the aniline, but mainly to the formation of condensation products of the amine and a decomposition product of the glucose.

Experimental Part

The following experiment gives an idea of the production of color in solutions of glucose and aniline containing acetic acid as compared with comparable blanks.

Fifty cc. of an ethyl alcohol solution of 1.5 g. of glucose, 0.775 g. (1 molecular proportion) of freshly distilled aniline and 0.5 g. (1 molecular proportion) of acetic acid

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[1] Nef, *Ann.*, **403**, 204 (1914).

[2] Harrison, This Journal, **36**, 586 (1914).

[3] Maillard, *Compt. rend.*, **154**, 66 (1912).

at room temperature (24–25°) became light yellow in two days, orange in 12, red in 18 and brown in 34. A comparable solution of glucose and aniline was a light yellow in 32 days and brown in 112. Similar solutions of aniline and acetic acid, and of aniline alone showed only a slight tinge of yellow in 120 days; at this time (120 days) a solution of glucose and acetic acid was still colorless.

In the acid solutions of glucose and aniline, the color remained brown, but after 90 days the solution failed to reduce Fehling's solution, showing that both glucose and glucose-anilide were not present as such. The alcoholic solution was then diluted to 400 cc. with water and the colored material, which separated, was filtered off and washed with water. After drying in a vacuum, it weighed 0.35 g. and had a very indefinite melting point (shrinking at 85°, black and glassy at about 116°, decomposing at 141°).

That glucose may react with aniline to form glucose-anilide[4] was recognized early in carbohydrate chemistry. Later, Irvine and Gilmour[5] proved that glucose-anilide has the butylene oxide structure and that it exists in two stereoisomeric forms, the α- and β-isomers. They further showed that the anilide is formed not only by heating glucose and aniline together in alcoholic solution, but that condensation takes place slowly when an ethyl alcohol solution of glucose is mixed with an excess of aniline and kept in the cold. A polarimetric examination of the process was thus possible. It was found that the initial dextrorotation of the solution at first increases steadily and then diminishes gradually, finally becoming constant when a decided levorotation is recorded. The initial rise, according to these authors, is due to the formation of the alpha isomer of dextrorotation; the subsequent fall is caused by the appearance of the beta isomer, the final product being essentially the *levo* isomer only. Further, they prove that the α-glucose-anilide is changed at once to the β-, on addition of a trace of acid. Finally, they point out that the anilide is readily hydrolyzed and that a methyl alcohol solution when heated with methyl iodide and silver oxide is vigorously oxidized.

Then, if the *dextro* isomer is first formed and gradually converted into the *levo* isomer, and if acid changes the former at once to the latter, it was thought that when aniline is allowed to react with glucose in the presence of an acid, the formation of the beta isomer should be hastened. It is found on following the reactions by means of the polariscope that this is true.

Thus two alcoholic solutions of 1.5 g. of glucose were made up and allowed to stand for 24 hours, so that the rotation might become constant. To one of these was added 0.5 g. (1 molecular proportion) of glacial acetic acid and to both 0.775 g. (1 molecular proportion) of freshly distilled aniline. The solutions were then made up to 50 cc. with ethyl alcohol, thoroughly mixed, and filtered into 1-dcm. polariscope tubes. Readings of the rotation were made as recorded in Table I, only the more pertinent observations being recorded. Time was computed from the addition of the aniline in all cases. After 12 days, readings on the acid solution were discontinued because of the color developed.

When glucose reacts with aniline alone, it is found that the initial dextro-

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[4] Schiff, *Ber.*, 4, 908 (1871).

[5] Irvine and Gilmour, *J. Chem. Soc.*, 93, 1429 (1908).

Table I

Effect of Acetic Acid on the Reaction between Glucose and Aniline

Glucose, 1.5 g. Aniline, 0.775 g. Solvent, 95% ethyl alcohol to a volume of 50 cc. Tube, 1 dcm. Temp., 20°.

Time	Acetic acid 0.5 g. α	No acid α
5 min.	+1.73°	+1.74°
1 hour	+1.10	+1.76
4 hours	−0.40	+1.77
6 hours	−0.72	+0.74
1 day	−1.22	+1.57
2 days	−1.25	+1.22
6 days	−1.21	−0.07
12 days	−1.15	−0.88
24 days	?	−1.26
28 days	?	−1.28
36 days	?	−1.23

rotation increases very slightly but there certainly is a distinct lag, as in six hours the rotation was identical with the initial reading. This agrees with the findings of Irvine and Gilmour[5] and is explained by these authors as due to the initial formation of the *dextro* isomer. In the presence of acid, this preliminary formation of the alpha isomer is not apparent; the rotation rapidly falls to its maximum value of —1.25° in two days. As the maximum value of —1.28° was observed in 28 days with glucose and aniline alone, the effect of acetic acid on the formation of the *l*-anilide is apparent providing, of course, that glucose-anilide is formed in the acid solutions.

That glucose-anilide is formed in acid solutions of glucose and aniline is shown by precipitating the anilide from such solutions by means of a mixture of ether and benzene. From other experiments, it was decided that it was best to use an excess of the reactants (3 molecular proportions) as with molecular quantities of aniline and acetic acid the formation of the anilide is far from complete.

Thus to a 3% alcoholic solution of glucose, which had stood for 24 hours, were added 11.62 g. of aniline (3 molecular proportions) and 7.5 g. of acetic acid (3 molecular proportions) and the volume was made up to 250 cc. with alcohol. The solution was allowed to stand at room temperature (23°) for 20 hours, when the rotation had fallen to its lowest negative value (−1.93°). The yellow solution was then cooled in an ice-salt mixture and a large excess of anhydrous ether and benzene (3 1) added. The precipitate that formed was removed by filtration, washed thoroughly with anhydrous ether and dried in a vacuum over paraffin. There was thus obtained 6.4 g (60% of that calculated on the basis of glucose-anilide) of a slightly yellow powder; m. p., 129–132°; $[\alpha]_D^{23}$ = —47.6° for a 3% solution in methyl alcohol. Glucose-anilide browns at 140° and melts at 147°.[6] The specific rotation in methyl alcohol[5] is recorded to be —52.3°.

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[6] Sorokin, *Ber.*, 20(R) 783 (1887).

The material was recrystallized four times by dissolving in absolute ethyl alcohol filtering while hot and precipitating cold with anhydrous ether. There was finally obtained 3.4 g. of a pure white material; m. p., 146°; $[\alpha]_D^{23}$ = —51.6° for a 3% solution in methyl alcohol.

Anal. Calcd. for $C_{12}H_{17}O_5N$: N, 5.49. Found: 5.26.

That glucose-anilide is responsible for the color in acid solutions of glucose and aniline is indicated by the fact that this substance in alcohol becomes colored and more rapidly so if acetic acid is present. Two solutions of a pure glucose-anilide were made up as in Table II below; the color of the solutions was noted and the rotation followed in order to determine the effect of acid.

The glucose-anilide was prepared in the usual manner;[6] it was recrystallized four times from methyl alcohol and washed with anhydrous ether. A 3% solution in methyl alcohol gave $[\alpha]_D^{22}$ = —52.22°.

TABLE II

ROTATION AND COLOR OF GLUCOSE-ANILIDE IN ETHYL ALCOHOL

Glucose-anilide, 2.125 g. Solvent, 95% ethyl alcohol to volume of 50 cc. Tube, 1dcm. Temp., 21°.

	No acid		Acetic acid, 0.5 g.	
Time	α	Color	α	Color
5 min.			−1.32	Colorless
30 min.	−0.72	Colorless	1.42	Colorless
1 day	1.47	Colorless	1.34	Slight yellow
4 days	1.37	Slight yellow	1.28	Decided yellow
6 days	1.35	Yellow	1.25	Orange
24 days	1.30	Decided yellow	?	Red-brown
47 days	?	Orange		

In the absence of acid, the solution of glucose-anilide gradually became more negative; according to Irvine and Gilmour[5] this is due to the conversion of the alpha to the beta isomer. The maximum value (—1.47°) was recorded in 24 hours; thereafter the slight rise in rotation was probably due to hydrolysis. With acid present, the maximum value (—1.42°) was noted in half an hour. This corroborates the findings of Irvine and Gilmour that the *d*-isomer is rapidly changed to the *l*- in presence of acid. Both solutions became colored but the acid solution much more rapidly than the other.

In 40 days the brown acid solution was diluted to 400 cc. with water and the colored precipitate removed. After drying in a vacuum, it weighed 0.26 g. and melted vaguely between 94° and 150°.

This simply indicates that from acid solutions of glucose-anilide a colored material can be obtained similar to that from an acid solution of glucose and aniline.

Finally, the effect of changing the concentration of aniline and of aniline and acetic acid was studied. In the case of aniline alone, the solutions were made up as given in Table III with acid present as in Table IV.

TABLE III

EFFECT OF INCREASE IN CONCENTRATION OF THE ANILINE ON THE PRODUCTION OF GLUCOSE-ANILIDE

Glucose, 1.5 g. Solvent, ethyl alcohol to volume of 50 cc. Tube, 1 dcm. Temp., 22°.

Aniline Time	4.65 g. 6-mol. proportions α	6.975 g. 9-mol. proportions α
5 min.	+1.73	+1.73
6 hours	+1.77	+1.78
1 day	+1.78	+1.73
6 days	−0.30	−0.39
12 days	−1.80	−1.94
20 days	−2.12	−2.23
21 days	−2.14	−2.25[a]
22 days	−2.17[a]	−2.25
23 days	−2.16	−2.23

[a] Maximum values observed.

Again at the start, using aniline and glucose, a slight increase in rotation is noted, presumably due to the formation of the alpha isomer. The effect is not so marked as that obtained by Irvine and Gilmour but they used a more concentrated sugar solution and a lower temperature (2–6°). After the first day the rotation gradually falls until in 21 and 22 days, respectively, the maximum values for the 6 and 9 molecular proportions of aniline was noted.

TABLE IV

EFFECT OF INCREASE IN CONCENTRATION OF ANILINE AND ACETIC ACID ON THE PRODUCTION OF GLUCOSE-ANILIDE

Glucose, 1.5 g. Alcohol to 50 cc. Tube, 1 dcm. Temp., 21°.

Aniline, mol. pro.	3	6	9
Acetic acid, mol. pro.	3	6	9
Time, hours	α	α	α
$^1/_{12}$	+1.52	+1.20	+0.93
1	−0.40	−1.57	−1.98
2	−1.28	−2.02	−2.10[a]
4	−1.80	−2.07[a]	−2.09
6	−1.92	−2.05	−2.07
24	−1.95[a]	−2.02	red
48	−1.90	red	
96	red		

[a] Maximum values observed.

With acid present, as before, the preliminary formation of the alpha isomer was not observed, the rotation rapidly falling to its maximum value. The effect of the acid in speeding up the reaction is very noticeable; for instance, using 6 moles of aniline alone, the maximum value was recorded in 22 days, while with 6 molecular proportions of acid and aniline the maximum value was noted in four hours. The effect of acid on the rate of reactions such as ester formation is, of course, well known. The interest in this particular case lies in the fact that reactions between amines, which are bases, and glucose can be speeded up by acids and at the same time the solution becomes neither basic nor strongly acid. It becomes, in effect, a reaction of glucose near the neutral point. This will be dealt with later.

A rough idea of the percentage formation of glucose-anilide under different conditions can be calculated by using the maximum rotations observed and the specific rotation of glucose-anilide in alcohol. The latter value was determined as follows in presence of excess aniline to prevent hydrolysis.

1.4998 g. of a pure glucose-anilide was dissolved in ethyl alcohol, 3.87 g. of aniline added and the volume made up to 50 cc. In 35 minutes, the rotation in a 1dcm. tube was +0.01°. This positive value is due to the presence of the alpha isomer, but as this is gradually converted into the beta, the rotation slowly falls, so that in 11 days a maximum value of —1.67° was recorded. Thereafter the rotation very slowly became less negative due to hydrolysis, but even in 30 days it was —1.62°. The maximum rotation gives $[\alpha]_D^{21}$ —53.01° for glucose-anilide in the presence of excess of aniline.

The calculated amount of glucose-anilide that could be formed from 1.5 g. of glucose and the requisite amount of aniline is 2.125 g., and this should give α, —2.25. The values obtained are given in Table V.

TABLE V

SPECIFIC ROTATIONS OF GLUCOSE-ANILIDE

Aniline, molecular proportions	Acid, molecular proportions	Max. $[\alpha]_D$ obs.	Glucose-anilide %
1	0	−1.28	56.9
6	0	−2.17	96.4
9	0	−2.25	100
1	1	−1.25	55.6
3	3	−1.95	86.7
6	6	−2.07	92.0
9	9	−2.10	93.3

Summary

Aromatic amines, such as aniline, act on glucose in the presence of acetic acid to produce a brown material that is insoluble in water. Likewise, glucose-anilide in the presence of acetic acid becomes colored to yield a similar product. As glucose-anilide is formed in acid solutions of glucose and aniline and as the formation of this compound is catalyzed by acid, it is believed that the initial step in the production of the colored material is the formation of glucose-anilide.

Glucose-anilide in ethyl alcohol containing an excess of aniline to suppress hydrolysis gave $[\alpha]_D^{21}$ = —53.01°.

The effect of using an excess of the reactants, aniline and acetic acid, on the formation of glucose-anilide is noted; unless an excess is used, the reaction is far from complete.

SASKATOON, SASKATCHEWAN

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

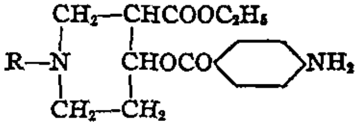
PIPERIDINE DERIVATIVES. III. 1-ALKYL-3-CARBETHOXY-4-PIPERIDYL PARA-AMINOBENZOATES

BY S. M. MCELVAIN

RECEIVED JUNE 15, 1926 PUBLISHED AUGUST 5, 1926

In a previous paper[1] the preparation and pharmacological properties of a series of 1-alkyl-3-carbethoxy-4-piperidyl benzoates were described. Some of these substances were quite active local anesthetics with very low toxicities. There was, however, an objectionable property encountered in their use in the fact that the aqueous solutions of their halogen acid salts showed an acid reaction to litmus. This property caused considerable irritation and hyperemia in the rabbit's cornea and, as was pointed out at that time, possibly tended to shorten the duration of anesthesia.

It seemed probable that this undesirable property would not be present in the 1-alkyl-3-carbethoxy-4-piperidyl *p*-aminobenzoates if they were used as the monohydrochlorides. Accordingly, a series of these substances with the general formula



was synthesized. This paper deals with the preparation and a preliminary pharmacological study of the compounds in which R is methyl, ethyl, *n*-propyl, *iso*propyl, *n*-butyl, *iso*butyl and *iso*-amyl.

The method of synthesis of these compounds was analogous to that which was used for the piperidyl benzoates,[1] except that *p*-nitrobenzoyl chloride instead of benzoyl chloride was used in the acylation of the 1-alkyl-3-carbethoxy-4-hydroxypiperidines. The piperidyl *p*-nitrobenzoates formed readily and offered no difficulties in crystallization.

The reduction of the nitro compounds to the corresponding amino derivatives was first accomplished by iron and hydrochloric acid. This procedure, however, was abandoned partly on account of low yields and mainly because catalytic reduction was found to be much more efficient for the conversion. The hydrochlorides of the *p*-nitrobenzoates in alcohol solution were completely reduced in a few minutes with Adams' platinum oxide-platinum black catalyst. Although this reduction yielded the monohydrochlorides directly, they were not isolated as such, but were converted into the dihydrochlorides because these salts were found to crystallize much more readily.

Experimental Part

1-Alkyl-3-carbethoxy-4-piperidyl *p*-Nitrobenzoate Hydrochlorides.—The amorph-

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[1] McElvain, THIS JOURNAL, 48, 2179 (1926).

ous residue obtained from the catalytic reduction of 10 g. of the 1-alkyl-3-carbethoxy-4-piperidone hydrochloride after the evaporation of the solvent was treated with 15 g. of *p*-nitrobenzoyl chloride. This mixture was heated in an oil-bath at 140–160° *until the evolution of hydrochloric acid ceased. The resulting solution was then* cooled, diluted with 200 cc. of ether and the oily precipitate allowed to crystallize in an ice box. This solidified precipitate was recrystallized from an alcohol-ether mixture. The yields were 50–70% of those theoretically possible from the piperidones.

Table I

1-Alkyl-3-carbethoxy-4-piperidyl *p*-Nitrobenzoate Hydrochlorides

Alkyl group	Formula	M. p., °C.	Cl, % Calcd.	Cl, % Found
Methyl	$C_{16}H_{21}O_6N_2Cl$	193–195	9.54	9.38
Ethyl	$C_{17}H_{23}O_6N_2Cl$	214–216	9.20	9.18
n-Propyl	$C_{18}H_{25}O_6N_2Cl$	206–208	8.87	8.81
*iso*Propyl	$C_{18}H_{25}O_6N_2Cl$	203–205	8.87	8.73
n-Butyl	$C_{19}H_{27}O_6N_2Cl$	192–194	8.55	8.68
*iso*Butyl	$C_{19}H_{27}O_6N_2Cl$	204–206	8.55	8.44
iso-Amyl	$C_{20}H_{29}O_6N_2Cl$	167–169	8.28	8.20

1-Alkyl-3-carbethoxy-4-piperidyl *p*-Aminobenzoate Dihydrochlorides.—A solution of 5 g. of the 1-alkyl-3-carbethoxy-4-piperidyl *p*-nitrobenzoate hydrochloride in 100 cc. of 95% alcohol and 0.25 g. of Adams' platinum oxide catalyst were shaken with hydrogen at 2–$2^2/_3$ atmospheres' pressure. The reduction began at once and proceeded with such vigor that the mixture became warm. The calculated amount of hydrogen was absorbed in five to ten minutes. The first reductions were carried out with 5 cc. of acetic acid in the alcoholic solution of the nitro compound for the purpose of combining with the amino group as soon as it was formed, but it was found that this procedure was unnecessary, for the reduction took place just as satisfactorily without the acetic acid as with it. The catalyst was filtered off and the filtrate evaporated nearly to dryness under diminished pressure. The residue was dissolved in water and the free base precipitated with sodium carbonate. This free base was extracted with ether and reprecipitated from the ethereal solution as the dihydrochloride with dry hydrogen chloride. This precipitate was first allowed to solidify in an ice box and then recrystallized from an alcohol-ether mixture. The yields were 60–80% of those calculated.

Table II

1-Alkyl-3-carbethoxy-4-piperidyl *p*-Aminobenzoate Dihydrochlorides

Alkyl group	Formula	M. p., °C.	Cl, % Calcd.	Cl, % Found
Methyl	$C_{16}H_{24}O_4N_2Cl_2$	190–192	18.73	18.52
Ethyl	$C_{17}H_{26}O_4N_2Cl_2$	204–206	18.06	17.89
n-Propyl	$C_{18}H_{28}O_4N_2Cl_2$	221–223	17.45	17.31
*iso*Propyl	$C_{18}H_{28}O_4N_2Cl_2$	196–198	17.45	17.30
n-Butyl	$C_{19}H_{30}O_4N_2Cl_2$	228–230	16.86	16.84
*iso*Butyl	$C_{19}H_{60}O_4N_2Cl_2$	230–232	16.86	16.67
iso-Amyl	$C_{20}H_{32}O_4N_2Cl_2$	213–215	16.32	16.10

Pharmacological Studies[2]

The dihydrochlorides were dissolved in water and titrated with sodium hydroxide to the point of precipitation of the free base in order to form the

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[2] The author is indebted to Mr. Ralph E. Jones of the Department of Pharmacology of the University of Wisconsin for these studies.

neutral monohydrochlorides. The durations of anesthesia and the toxicities were determined with the monohydrochloride solutions in the same manner as described for the 1-alkyl-3-carbethoxy-4-piperidyl benzoates. These *p*-aminobenzoates produced toxic symptoms similar to those of cocaine.

Table III

Pharmacological Data

	Duration of anesthesia with 2% soln., min.				Toxicity to white mice, mg per kg. body weight		
Alkyl group	Individual expts.			Av.	No of mice	Max. tol. dose	Minimum lethal dose
Methyl	23	27	27				
	25	21		26	9	50	100
Ethyl	37	33	33				
	36	29	35	34	10	150	200
n-Propyl	33	36	33				
	37	34		35	17	200	250
*iso*Propyl	33	33	30				
	44	47	23	36	13	100	150
n-Butyl	32	53	37				
	33	55	43				
	40	43		43	34	450	550
*iso*Butyl	40	45	36				
	41	50	23	39	16	450	550
iso-Amyl	65	39	100				
	30	76	73				
	62	77		72	25	500	550
Cocaine	36	31	28				
	24	33	29				
	24	32	29	29	18	100	150

Discussion of the Pharmacological Data

From the above pharmacological report it is seen that the members of this series of piperidine derivatives exhibit the variations in physiological action that were noticed in the case of the 1-alkyl-3-carbethoxy-4-piperidyl benzoates. In both cases an increase in the size of the alkyl group attached to the piperidine nitrogen caused an increase in the duration of anesthesia and a decrease in toxicity. The members of the *p*-aminobenzoate series, however, showed decidedly greater durations of anesthesia and higher toxicities than the corresponding benzoates. The increase in anesthesia is probably explained in part by the fact that the solutions of the monohydrochlorides of the *p*-aminobenzoates that were used in the tests were neutral to litmus and caused no irritation or hyperemia in the rabbit's cornea. It does not seem possible to explain the increase in the toxicities at present, but it is hoped that future work will point to an explanation of this observation.

It is interesting to note that the 1-*iso*-amyl-3-carbethoxy-4-piperidyl *p*-aminobenzoate shows two and one-half times the anesthetic power and about one-fourth the toxicity of cocaine.

Summary

1. A series of 1-alkyl-3-carbethoxy-4-piperidyl *p*-aminobenzoates have been prepared and some of their properties noted.

2. These substances are local anesthetics. They show an increase in anesthetic action and a decrease in toxicity as the size of the alkyl group in the 1 position is increased. The *iso*-amyl derivative possesses two and one-half times the anesthetic power and about one-fourth the toxicity of cocaine.

MADISON, WISCONSIN

NOTE

The Melting Point of 4-Chloro-2,6-dibromo-aniline.—It was found necessary to prepare this compound in the course of an investigation recently undertaken and the melting point is recorded in the literature differently by different investigators; 97°[1] and 95°.[2] The melting point obtained by us was still different, so extreme care was used in establishing the correct temperature.

The compound was prepared by the bromination of pure *p*-chloroaniline (m. p., 71–72°) obtained from three different sources. Bromination was carried out both in aqueous solution and in glacial acetic acid. The compound was then recrystallized variably from dil. alcohol, absolute alcohol or glacial acetic acid. Four recrystallizations failed to change the melting point. The temperature was measured with two recently calibrated thermometers, one having a short stem with practically no stem correction. The melting point was established both by the cooling curve of a quantity of the material and by the usual method using a small tube. In every instance it was 92.9°, corrected.

It is believed that this should be reported since the melting points of the isomeric chlorodibromo-anilines are very close together, and the melting point in question is at present in considerable error.

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[1] Chattaway and Orton, *J. Chem. Soc.*, **79**, 816 (1901).

[2] Zincke, *Ann.*, **333**, 338 (1904).

NEW BOOKS

Chapters in the History of Science. General Editor, CHARLES SINGER. III. Chemistry to the Time of Dalton. By E. J. HOLMYARD. Oxford University Press, American Branch, New York, 1925. 128 pages. Illustrated. 19 × 12 5 cm. Price $1.00.

The history of chemistry is generally divided into four periods: the Egyptian, the Islamic, the Early European and the Modern periods. The first three are generally designated as alchemistic and reflect Greek influence. It is the author of this new volume, Holmyard, who has recently done us great service by bringing light into the darkness of the Islamic period, teaching us facts which Berthelot never knew and could not know. He has persuaded us that Geber—the first and master-mind of Islamic chemistry—is to be ranked with Lavoisier in his teaching and influence. Pleasant also it is to learn something tangible of Maslama, known as al-Magriti, and of Abu'l Qasim, called al-Iraqi—those famous authors, known previously only in name, who formed the link between the Arabic and the Spanish. Perhaps, as the author suggests, we may soon be able to outline an evolution of the science of chemistry.

I confess to a little disappointment in the present book, in that the author's own field is so little represented: only about fifteen pages. An author is quite safe on his own ground and no one can teach us better the facts of Islamic chemistry than one who has mastered the difficult Arabic, one whose privilege it is to unfold for us the very words of these authors of the Mohammedan period, closed to us heretofore. Like the tomb of Tut-enkh-amen we have, in the Arabic, a treasure house in which is being revealed a craftsmanship and wealth unsuspected.

Why is it that our British cousins are so slow in recognizing the value of the work of Berthelot on Egyptian alchemy? Our author tells us, as though he were writing before 1885, that in the city of Alexandria "alchemy was studied mainly as an offshoot of magic;" also that Jabir's views "represent a distinct advance....upon the incomprehensible mysticism of the Alexandrian school." It is difficult to follow, also, when our author tries to establish the blanket priority of the Mohammedan school. A proof seems necessary that the predecessors of this school contributed nothing. The theories of Jabir, we are told, were a modified Aristotelianism; but so were the Alexandrian theories—five centuries before. The mercury-sulfur composition of the metals came directly from Egypt. Except for the clear statement of this composition, as a working theory, nearly all the ideas and experiments of Jabir, as quoted, seem to reflect the ideas and (perhaps cruder) experimental work of the Alexandrians. Again, the word obscurity, as applied to Egyptian alchemy, was only yesterday in common use as regards Geber and his successors. This latter obscurity it has been the privilege of Holmyard to clear away. The fact is that obscurity is a relative term and we have to guard against the possibility of its being wholly subjective. In the present case, we can not close our eyes to certain wonderful things which Alexandrian Greeks transmitted to the Court of Harun al-Rashid.

But to return to our text, the chapters which follow the Mohammedan period, "Chemistry in Europe" and "From Norton to Glauber," tell the story of European alchemy and its derivation from Arabian sources in simple and straightforward language. We are carried easily to the seventeenth century, to the development of the phlogiston theory, with the trenchant comments of Boyle, to the short, tragic, but impressive life of "Phlogiston," until "by the irony of fate, it was largely through discoveries made by eminent phlogistonists themselves that their theory was finally overthrown"—due to the interpretation of these discoveries by Lavoisier.

The author closes his little but distinguished book with the thesis that modern chemistry is founded upon the two theories of Lavoisier and Dalton: the "foundations of modern science were laid by Antoine Laurent Lavoisier and John Dalton. They are the oxygen theory of combustion and the atomic theory of the constitution of matter—the brightest achievements of the human intelligence."

Holmyard is a ready and facile writer and carries the reader delightfully along through the whole story. Since the book is a history of chemistry rather than a history of alchemy, it is proper that more than one half should be devoted to discoveries made since the beginning of the seventeenth century, for although the phlogiston theory and all the writers up to the time of Lavoisier reflected the Greek attitude of "forms," it was upon the exact materialism of Boyle and the incontrovertible demonstrations of Black, as interpreted by Lavoisier, that the quality-elements of the Greeks and the "tria principia" of Paracelsus were overthrown and the material element established.

Extracts from epoch-making writings embellish the book—just enough of these to illustrate the argument and clarify the thought.

I note that the author promises a second volume, to tell us the theory of Avogadro and "the entrancing story of the progress which chemists, on the basis of the atomic theory, were able to make in the nineteenth century." Readers will await with interest the appearance of this account of how our fathers used this "golden key to the treasures of nature—of which the full extent is even yet not more than dimly perceived."

ARTHUR JOHN HOPKINS

First Problems in Chemistry. By MARTIN MEYER, Ph.D., Instructor in Chemistry, The College of the City of New York. D. C. Heath and Company, Boston, 1925. vii + 300 pp. 17 figs. 13 × 19 cm. Price $1.60, postpaid.

Few chemists, if any, will disagree with the author of this book in emphasizing the importance of chemical calculations. The calculations, however, which are dealt with in "First Problems in Chemistry" are the simplest of arithmetic applied to chemical relations, and certainly involve no special kind of mathematics, as the existence of such books as this might imply. In other words the demands of chemical calculations differ from those of other arithmetical problems only in the knowledge of chemistry required and in the ability to make the necessary application. The principles of chemistry involved are presented in all elementary texts, for which the book under consideration serves as an unnecessary auxiliary, not as a substitute.

The student's knowledge of the applications is apt to become merely the trick of substituting the proper numbers in a memorized formula. When this is the case, one of the chief values of chemical calculations, practice in reasoning, is lost. The segregation of calculations in a book by themselves seems to emphasize this tendency to make the subject unrelated to actual substances and conditions and to make the solutions of the problems only exercises in arithmetic. In short, why use special books on chemical calculations?

If, however, such books are to be used, "First Problems in Chemistry" is an excellent choice. It contains over six hundred problems and several hundred questions. These include problems in stoichiometry, on the behavior of gases, on the boiling and freezing temperatures of solutions and their relations to ionization, and on the use of "normal solutions." Since the statements of the problems occupy but a few pages, the most of the three hundred pages of the book are devoted to discussion of principles and laws.

One looks in vain for any mention of "significant figures" and the principle of "proportional error." The expositions and the derivations of formulas are detailed but clear, and necessarily "dry." If a student can be made to swallow and assimilate such a dose, it will be good for his constitution in these days when youth must be pampered with "interesting" information only. The large number of problems and questions will be appreciated by teachers weary of setting tests and examinations.

Kenneth L. Mark

Atomzertrümmerung: Verwandlung der Elemente durch Bestrahlung mit α-Teilchen. (Atomic Disruption; Transmutation of the Elements by α-Radiation.) By Hans Pettersson and Gerhard Kirsch. Akademische Verlagsgesellschaft m. b. H., Leipzig, 1926. viii + 247 pp. 61 figs. 24.5 × 16 cm. Price, unbound, Mk. 13; bound, Mk. 15.

Modern science, not content with penetrating the atom and dissecting it electron by electron, does not halt at the threshold of the nucleus itself but is now battering its way into that "holy of holies" of the atom. The projectile used is the most powerful agent known—the high speed alpha particle, itself ejected with tremendous energy from the nucleus of radioactive elements. The product of one atomic disintegration is thus directed to expend its energy in disrupting another nucleus.

Pettersson and Kirsch have given in monograph form an illuminating account of the researches in this field. The work has been practically confined to two laboratories, that of Sir Ernest Rutherford at Cambridge, where it was begun, and the Institute of Radium Research in Vienna, where it was taken up by Pettersson and his collaborators, who have added many valuable contributions in its continuation.

The subject is developed beginning with recognition by Rutherford of the significance of the rarity of large angle deflections or reversals of alpha particles projected through atoms. This gave us Rutherford's conception of the nuclear atom. The next step was the production of swift hydrogen particles by bombarding hydrogen or its compounds by alpha particles. The rarity of the ejection of hydrogen particles confirmed the nuclear hypothesis. The next great stride, which led into the nucleus itself, was the discovery that hydrogen particles can also be produced by bombarding atoms of other elements. This possibility was at first believed to be confined to six elements of odd atomic number—boron, nitrogen, fluorine, sodium, aluminum and phosphorus. The method of indirect or right-angle observation developed by Pettersson and his associates at Vienna has permitted the detection of very short range hydrogen particles which has extended the list of elements disrupted to include of odd-numbered atoms—chlorine, argon, copper, bromine and iodine, and of even-numbered elements—sulfur, potassium, titanium, chromium, iron, selenium, zirconium, tin and tellurium. Of the total disruptions 11 were first effected by Rutherford and Chadwick and 16 by Pettersson, Kirsch and co-workers.

The entire theme of atomic disintegration is skilfully developed in eight chapters giving detailed accounts and summaries of the work both at Cambridge and Vienna. The use of thin capillaries containing radon has proved to be a convenient source of alpha-radiation which removes the difficulty of diffusion of radon from an open source. This method, combined with indirect observation, has yielded many fruitful results. It was also employed to investigate truly "induced radioactivity" in other elements. The result was negative.

While the outer electronic structure of the atom is of primary importance to the chemist, since it touches his valence electrons and through them determines the structure of the compounds of the elements and their chemical properties, the structure of the nucleus is no less important since it touches the elements themselves. The interest attaching to the conservation of the elements and to their transmutation is one of the oldest in chemistry, which has received a tremendous revival through the researches initiated in the disruption of the atom by alpha particles. The writers do not discuss, however, the recent experiments directed toward transmutation. A most useful appendix is one of four pages giving a condensed chronological and historical review of the subject. Atomic disruption merits the attention of all those interested in the most modern developments of physical science. Pettersson and Kirsch have, therefore, rendered a service of the first order in so admirably bringing together the results accomplished up to the present and in furnishing a basis for further progress by presenting a lucid account of their own experimental achievements.

S. C. LIND

Thermochimie. (Thermochemistry.) By F. BOURION, Professor of the Faculty of Sciences at Nancy, Libraire Octave Doin, 8 Place de l'Odéon, Paris, 1924. xii + 363 pp. 43 figs. 13.5 × 22 cm. Price, unbound, 25 fr.

This work covers the same general field as the first volume of Berthelot's "Thermochimie," and from largely the same point of view. After a clear discussion of the first law, the methods of calorimetry are taken up giving, as is good pedagogical practice, much space to the old and primitive methods of Berthelot and then skipping to modern methods especially those of White, Barry and Richards. Only enough detail is given to show the essence of the method. A particularly valuable feature of the book is the discussion of the method of determining thermal quantities by use of the second law of thermodynamics. However, to the reviewer's mind, the treatment of the so-called "third law," which is at least as important in this connection, is quite inadequate. Indeed, excepting for the treatment of the second law, one would get the impression that no great progress had been made in thermochemistry since the time of Berthelot. For example, comparatively little use is made of the ionic theory; the lattice energy concept of Born and Fajans is hardly mentioned; the quantum theory with its connection between spectroscopy and thermochemistry is omitted; even the subject of heat of dilution, the connection of which with the theory of solution was pointed out by Berthelot, is treated in a summary manner. Nevertheless, the book is to be recommended especially for student use since it gives the only elementary, yet relatively complete, introduction to the methods and concepts of thermochemistry at present available, presented with the clarity and elegance expected in a French work. It is regretted that we do not have more works of this class in English.

F. RUSSELL BICHOWSKY

The Production and Measurement of Low Pressures. By F. H. NEWMAN, D Sc., Professor of Physics in the University College of the Southwest of England, Exeter. Ernest Benn Limited, 8 Bouverie Street, E. C. 4, London, 1925. 192 pp. 48 figs. 15 × 24 cm. Price 16s net.

This book contains a valuable compendium of information for the practical worker with high-vacuum technique. A brief discussion of the theory of pumps and of the flow of gases at low pressures is followed by descriptions and tables of performance of some 20 different pumps, well selected to represent the various types that have been found most efficient for particular purposes. The theory of the mercury diffusion pump is treated at some length, but not, it seems, with complete lucidity. Extensive data are included on the preparation and use of charcoal for producing vacuums, and a chapter is devoted to the somewhat mysterious process by which a glowing tungsten filament destroys residual gases, and to various chemical and electrical methods of improving vacuums. Possibly the most useful chapters are the last two, which treat, respectively, of the principal modern designs of micromanometers, and of the practical operation of a high-vacuum system, which means essentially the methods of eliminating or controlling the evolution of gases from the glass surfaces, a phenomenon very puzzling and discouraging to any one using a good pump for the first time.

Albert Sprague Coolidge

The Kinetics of Chemical Change in Gaseous Systems. By C. N. Hinshelwood, M.A., Fellow of Trinity College, Oxford. Oxford University Press, American Branch, New York, 1926. 204 pp. 9 figs. 24.5 × 16 cm. Price $4.25.

This volume contains seven chapters. The first is an Introduction, setting forth in simple fashion those developments of the kinetic theory of gases which are of special utility in the kinetics of gaseous reactions. The titles of the other chapters are as follows: Bimolecular Reactions; The Energy of Activation; Termolecular Reactions; Unimolecular Reactions; The Kinetics of Heterogeneous Reactions; Activation in Heterogeneous Reactions.

The book has been developed from a series of lectures given in Oxford by the Author. It is not a comprehensive treatise but rather a brief and interesting survey of an important field of theoretical chemistry, in which the Author has himself been productively active. The presentation is straightforward and clear, with as little emphasis as possible on the mathematical operations. On the other hand, the Author has successfully resisted the temptation toward over-simplification. The book will be read with pleasure and profit by those interested in this rapidly developing field.

Arthur B. Lamb

Fortschritte der Kolloidchemie. (Advances in Colloid Chemistry.) By Professor Dr. Herbert Freundlich, Member of the Kaiser Wilhelm-Institute for Physical Chemistry and Electrochemistry, Berlin-Dahlem. Theodor Steinkopff, Dresden-Blasewitz, Residenzstrasse 12 b, 1926. ii + 109 pp. 47 figs. 22.5 × 14.5 cm. Price, unbound, M. 5.50.

This small volume is based on the lectures which Professor Freundlich delivered at various universities in the United States, during the summer of nineteen hundred and twenty-five. The titles of its eight chapters are: Adsorption; Electrokinetic Potential; Adsorption, Valence and Coagulation; Velocity of Coagulation; Stability of Hydrophilic Sols; The State and Form of Colloid Particles; The Absolute Magnitude and the Variability of Interfacial Surface in Colloidal Systems; Photodichroism and Related Phenomena.

These chapters are brief surveys of the recent progress in their various fields. They constitute, as it were, a partial supplement to the Author's invaluable "Kapillarchemie." As the Author points out, they show in a marked fashion how the progress of science consists of a series of closer and closer approximations. Our ideas of adsorption, of electrokinetic potential, of coagulation and of the shape of colloidal particles, for instance, have become progressively more sharply defined as a result of the investigations recounted in this volume.

These chapters not only fulfil admirably their function as surveys but they are also rich in suggestions for further research. They will be read with particular pleasure by those who were fortunate enough to hear the original lectures as given by Professor Freundlich.

Arthur B. Lamb

Chemische Bodenanalyse: Methoden und Anleitung zur Untersuchung von Böden im Laboratorium. (The Chemical Analyses of Soils: Methods for and Introduction to the Investigation of Soils in the Laboratory.) By K. K. Gedroiz, Professor at the Forstinstitut in Leningrad. Translated into German from the Russian by Dr. L. Frey, Riga, Laboratorium des Katasteramts. Gebruder Borntraeger, W. 35 Schöneberger Ufer 12a, Berlin, 1926. xii + 245 pp. 8 figs. 25.5 × 16.5 cm. Price G. M. 12.

This book is a laboratory manual for the chemical analysis of soils. While alternative methods are given for determining certain constituents, the book is not a comparative study of the various methods that have been more or less widely used in different countries but is a collection of selected methods. American literature on soil analysis evidently has been quite thoroughly examined and many American methods have been selected. It is rather surprising, however, that some of the methods of the Official Agricultural Chemists have not been included "as is," and that so little mention is made of Hillebrand's work on silicate analysis.

The various procedures are described in ample detail and comments are not lacking, although they are not a prominent feature of the book. Probably most chemists would have welcomed more extended remarks concerning the various methods; but in some cases the author has said about all there is to say in a few words. Regarding the acid digestion of soils the author points out: "What the ten per cent. hydrochloric acid really extracts from the soil, what compounds it dissolves and decomposes, we do not know."

The methods described cover the ultimate or "bulk" analysis of soils after decomposition by hydrofluoric acid or by alkali fusion, analysis of soils by acid extraction, analysis of the water extract, and investigation of the soil solution. Methods for determining some of the rarer constituents of soils, such as lithium and rubidium, are included and special chapters are devoted to colorimetric determinations, to the adsorbing soil complex, and to lime requirement methods. In the chapter on the lime requirement of the soil, fourteen different methods are described. Probably some of the sixteen other existing methods which are not mentioned are just as good as those that are described, but the inclusion of fourteen is enough to show that this is not an exact determination. The omission of methods for determining the Sörensen (*P*H) value of the soil, however, is a real lack, for in recent years this has been more widely used in soil investigations than any other single determination. The chapter on the determination of the adsorbing complex of the soil (we would call it "colloidal material)" is largely original material and is treated quite differently from the chapters on the older analytical methods. This chapter is especially welcome. The book should be well received as a whole although, needless to say, few chemists will accept all the procedures as being the best.

P. L. GILE

The Chemistry of Wheat Flour. By C. H. BAILEY, Ph.D., Professor of Agricultural Biochemistry in the University of Minnesota. American Chemical Society Monograph Series. The Chemical Catalog Company, Inc., 19 East 24th Street New York, 1925. 324 pp. 21 figs. 23.5 × 15.5 cm. Price $4.00.

This is one of the series of the monographs of the American Chemical Society. It is a pioneer book in its field and is the fruit of years of work by the author with wheat and flour. The author gives a résumé of the most important articles bearing on the chemistry of wheat flour. The scope of the book can be seen from the chapter headings: Historical; Wheat in its Relation to Flour Composition; The Growth and Development of the Wheat Plant and Kernel; Influence of Environment on the Chemical Composition of Wheat; Defects of and Impurities in Commercial Wheat; Chemistry of Roller Milling; Changes in Flour Incidental to Aging; The Color of Flour and Flour Bleaching; Flour Strength and Enzyme Phenomena; Flour Strength as Determined by the Proteins of Flour and Colloidal Behavior of Dough.

Wheat flour is composed of the same chemical constituents that are found in wheat, but in somewhat different proportions. The quality of wheat is largely determined by the environment in which it grows and develops. Enzymes in the wheat kernel are stimulated by temperature and moisture, hence these are the most important factors affecting wheat during storage. The wheat kernel consists of three main parts: bran coat, germ and endosperm. In milling, these are separated and, as these parts differ in chemical composition, the composition of the flour, particularly the ash or mineral content, will be affected by the condition of the milling process.

Flour undergoes changes during storage, improving for a time, and then there is a slow decrease in quality. The rate of these changes depends on moisture and temperature. The yellow or creamy color in flour is due to a natural pigment, the dark or gray color to accidental bran specks which fail to be separated in milling. The former color may be removed by bleaching, which process also has a maturing effect. The quality of wheat flour is measured by its response to the conditions of the bake shop. The most distinctive compound in wheat flour is the protein which forms gluten when water is added. Protein is a colloid and colloidal phenomena are helpful in understanding the chemistry of flour.

Probably the most valuable feature of the book is the comprehensive review of the literature on the chemistry of wheat flour, and the bibliography. These will be especially helpful to all research workers in cereal chemistry. Flour chemistry is of rather recent development, and the results obtained by various investigators have not been so well thought through and so systematically arranged as the data in several other lines of applied chemistry. This is a defect of youth in any branch of science and especially in a pioneer work. In future editions it would be well if the author would give more of his own thought and interpretation even if this will have to be done at the expense of omitting some less important data. The book will be of great value to all interested in the chemistry of wheat flour.

C. O. Swanson

Mitteilungen aus dem Schlesischen Kohlenforschungs-Institut der Kaiser-Wilhelm-Gesellschaft in Breslau. (Contributions from the Silesian Coal Research Institute of the Kaiser-Wilhelm Society in Breslau.) By Professor Dr. Fritz Hofmann, Director. Second volume. Gebrüder Borntraeger, Berlin, 1925. ii + 250 pp. 5 figs. 24.5 × 16 cm. Price, bound, Gm. 19.50.

Germany has three coal research institutes, each situated in one of the three principal coal fields, namely, The Kaiser-Wilhelm Institute for Coal Research in Mülheim-Ruhr, Franz Fischer, Director; The Silesian Coal Research Institute in Breslau, Fritz Hofmann, Director; and The Institute for Brown Coal Research in Freiberg, Saxony. Even though these institutes receive their financial support from the coal mining interests, they devote the major portion of their energies to fundamental research on coal and its products, and science is indebted to them for many valuable contributions on the constitution and origin of coal, the constitution of primary tar, and the catalytic reactions of gases from coal at various temperatures and pressures.

Although the Silesian Coal Research Institute was not completed until March 1922, it has already established itself as equal in quality of research output, if not in quantity, to that of the two older research institutes. Dr. Fritz Hofmann, the Director, is an able organic chemist who has won distinction by his successful researches on the synthesis of rubber, and more recently by the extraction of 500 kg. of an Upper Silesian coal with pyridine, and identifying a number of hydrocarbons in this extract.

The first and most important paper in this second volume of contributions from the Silesian Institute is Hofmann and Damm's second paper on the examination of the pyridine extract. It covers the neutral oils boiling above 300° including the solid paraffins, and the saturated and unsaturated hydrocarbons. Some thirty compounds were isolated and identified.

The second paper, by Hofmann and Heyn, on the solid phenols in primary tar gives a further definite contribution to our knowledge of the constitution of coal in proving that certain solid phenols found in the pyridine extract of coal may also be obtained in primary or low temperature tar if the coal is destructively distilled at the lowest possible temperature. Overheating results in liquid phenols only.

The third paper on the application of the Bergius process to the hydrogenation of coal tar gives the results of a well-conceived and carefully carried out examination of the hydrogenation products of a gas works tar and a coke oven tar. This paper is of interest both from the practical standpoint of making light oils from tar and from the theoretical point of view of the constitution of coal tar.

Papers 4, 5 and 6 also relate to the origin and constitution of coal, and are studies on polymerization processes. According to Hofmann, these have undoubtedly played an important role in the formation of coal. Two researches are reported, namely, on the action of sodium ethylate on the diethyl ester of 1,4-dibromo-adipic acid and on the polymers of the esters of muconic acid, by Kurt Vogt; and on Δ-1,3-dihydrobenzene, its derivatives and its polymerization products, by Fritz Hofmann and Paul Damm.

Lack of space prevents referring to each of the 15 papers in detail. All are well worth the attention of the coal chemist and many of them will interest the organic chemist as well. The by-product and petroleum chemist will want to read Dunkel's paper on the purification of crude benzol by polymerizing the gum-forming constituents through heating under pressure, and heating in the presence of oxygen, instead of the usual drastic acid treatment which causes a loss of useful and harmless unsaturated constituents.

The book is well bound and the paper and print are of excellent quality.

A. C. Fieldner

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Divisions—Agricultural and Food: E. F. Kohman, Chair.; C. S. Brinton, Sec., Food Insp. Lab., U. S. Appraisers Stores, Philadelphia, Pa. *Biological:* R. J. Anderson, Chair.; J. J. Willaman, Sec., Univ. Farm, St. Paul, Minn. *Cellulose:* H. LeB. Gray, Chair.; L. F. Hawley, Sec., Forest Prods. Lab., Madison, Wis. *Chemical Education:* Wilhelm Segerblom, Chair.; B. S. Hopkins, Sec., Univ. of Illinois, Urbana, Ill. *Dye:* R. Norris Shreve, Chair.; O. E. Roberts, Jr., Sec., 813 Ingraham St., Washington, D. C. *Fertilizer:* F. B. Carpenter, Chair.; H. C. Moore, Sec., Armour Fertilizer Works, 209 W. Jackson Blvd., Chicago, Ill. *Gas and Fuel:* S. W. Parr, Chair.; O. O. Malleis, Sec., 333 Melwood St., Pittsburgh, Pa. *Industrial and Engineering Chemistry:* W. A. Peters, Jr., Chair.; E. M. Billings, Sec., 484 Woodbine Ave , Rochester, N. Y. *Leather and Gelatin:* J. Arthur Wilson, Chair.; Arthur W. Thomas, Sec., Dept. of Chem., Columbia Univ., New York City. *Chemistry of Medical Products:* H. A. Shonle, Chair.; Arthur W. Dox, Sec., Parke, Davis & Co., Detroit, Mich. *Organic:* M. T. Bogert, Chair., Frank C. Whitmore, Sec., Northwestern University, Evanston, Ill. *Petroleum:* R. R. Matthews, Chair.: G. A. Burrell, Sec., Columbia Bank Bldg., Pittsburgh, Pa. *Physical and Inorganic:* H. B. Weiser, Chair.; G. L. Clark, Sec., Res. Lab. of Applied Chem. Mass. Inst. of Tech. Cambridge, Mass. *Rubber:* J. M. Bierer, Chair.; Arnold H. Smith, Sec., 462 Drexel Ave., Glencoe, Ill. *Sugar:* W. B. Newkirk, Chair.; Frederick J. Bates, Sec., Bureau of Standards, Washington, D. C. *Water, Sewage & Sanitation:* F. W. Mohlman, Chair.; F. R. Georgia, Sec., Rollins College, Winter Park, Fla.

Local Sections (Correct to date so far as reported to the Secretary of the Society. Sectional officers please note.)—*Akron.* R. P. Dinsmore, Chair.; W. J. Kelly, Sec., Goodyear Tire & Rubber Co., Akron, O. *Alabama:* R. W. Allen, Chair.; R. T. Pittman, Sec., 1018 28th St., S., Birmingham, Ala. *Ames:* N. A. Clark, Chair., J. A. Schulz, Sec., 306 Chemistry Bldg., Ames, Iowa. *Arizona:* T. F. Buehrer, Chair.; Lila Sands, Sec., Dept. of Chem., Univ. of Arizona, Tucson, Ariz. *California:* Herman A. Spoehr, Chair.; L. Rosenstein, Sec., 112 Market St., San Francisco, Calif. *Central Pennsylvania:* Gerald L. Wendt, Chair.; G. C. Chandlee, Sec., State College, Pa. *Central Texas*: W. T. Gooch, Chair.; G. S. Fraps, Sec., College Station, Tex. *Chicago:* P. N. Leech, Chair.; Lee F. Supple, Sec., Lewis Institute, Madison and Robey Sts., Chicago, Ill. *Cincinnati:* Geo. D. McLaughlin, Chair.; F. C. Vibrans, Sec., 234 Hosea Ave., Cincinnati, Ohio. *Cleveland:* John D. Morron, Chair.; N. A. 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The Coca Cola Co., Atlanta, Ga. *Hawaiian Section:* W. T. McGeorge, Chair ; R. Q. Smith. Sec., Lane 2341 North King St., Honolulu, T. H *Indiana:* Paul Smith, Chair., Neil Kershaw, Sec., 951 W 20th St.. Indianapolis, Ind *Illinois-Iowa:* H. L. Parr, Chair.: W Hinde. Sec., Box 188, Moline, Ill. *Iowa:* Jacob Cornog, Chair.: J. L. Whitman. Sec., 1025 E. Washington St , Iowa City, Iowa. *Kansas City:* Henry E Hancock, Chair.; A. S. Barada, Sec., 2018 Guinotte St., Kansas City, Mo. *Lehigh Valley:* C. L Nitchie, Chair.; H A. Nelson, Sec., New Jersey Zinc Co., Palmerton, Pa. *Lexington:* G. D. Buckner. Chair.; V F. Payne, Sec., Translyvania College, Lexington, Ky *Louisiana:* F. W. Liepsner, Chair.; Herbert O'Donnell, Sec., Room 324, U. S Custom House, New Orleans, La. *Louisville:* Frank M. Shipman Chair . Edward. R. Walsh, Sec., 605 E. Chestnut St., Louisville, Ky. *Maine:* Carl Otto, Chair.; Rudolph Macy, Sec., Box 364, Orono, Maine. *Maryland* L. H. Ingham, Chair., W. C. 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COMMITTEES

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Advisory to the Bureau of Mines and Bureau of Standards on Non-ferrous Metals: Wm. B. Price, Society's Representative, Scoville Mfg. Co., Waterbury, Conn

Advisory to the War Department: (Est 1922.) Chas. L. Parsons, 1709 G St., N. W., Washington, D. C. *Chairman*, H. E. Howe, Andrew Stewart.

Annual Report on Atomic Weights: (Est. 1897.) G. P. Baxter, Coolidge Memorial Laboratory, Cambridge, Mass

Chemical Education: (Est. 1923.) Neil E. Gordon, University of Maryland, College Park, Md., *Chairman*, B. S. Hopkins, D. B Keyes, L W. Mattern, L. C. Newell, R. E. Rose, W. Segerblom, T. G. Thomson, R. E. Swain, F. B Wade, F W. Willard.

Chemical Engineering Education: (Special) (Est. 1926) S. W. Parr, Urbana, Ill., *Chairman*, G. J. Esselen, D. B. Keyes, G. L. Wendt, F. W. Willard.

Coöperation with Chemical Warfare Service: (Est. 1920.) H. E. Howe, *Chairman*, Mills Bldg., N. W., Washington, D. C.; *Research*, W. D. Bancroft, E. P. Kohler, A. B. Lamb, G. A. Richter; *Development*, F. M. Dorsey, W. K. Lewis, L. T. Sutherland; *Production*, Bradley Dewy, L. C. Jones, C. L. Reese, W. H. Walker; *Physiological*, Reid Hunt, A. S. Loevenhart, Julius Stieglitz.

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Entrance Requirements: (Est. 1924.) E. R. Weidlein, Mellon Institute, Pittsburgh, Pa., *Chairman*, G. J. Esselen, H. R. Moody, H. B. Weiser, Frank C. Whitmore.

Exchange: (Est. 1907.) E. J. Crane, Ohio State Univ., Columbus, Ohio, *Chairman*, H. E. Howe, A. B Lamb.

Executive: (Est. 1923.) James F. Norris, 405 Marlborough St., Boston 17, Mass., *Chairman*, L. H. Baekeland, C. L. Parsons, J. E. Teeple, A. B. Lamb, H. E Howe, E. J. Crane. *Term expires December, 1926:* Geo. D. Rosengarten. *Term expires December, 1927:* Wm. McPherson. *Term expires December, 1928:* A. M. Comey.

Finance: (Est. 1893.) John E. Teeple, 50 E. 41st St., New York City, *Chairman*, F. G. Zinsser, F. J. Metzger.

Guaranteed Reagents: (Est. 1917.) W. D. Collins, U. S. Geological Survey, Washington, D. C., *Chairman*, H. V. Farr, Joseph Rosin, G. C. Spencer, Edward Wichers.

Hazardous Chemicals and Explosives (To Coöperate with National Fire Protection Association's Committee on the same subject): (Est. 1923.) C. E. Munroe, Forest Glen, Md., *Chairman*, H. LeB. Gray, A. H. Nuckolls, J. A. Rafferty, F. C. Zeisberg.

Historical Program Fiftieth Anniversary: (Est. 1925.) C. A. Browne, Bureau of Chemistry Washington, D. C., *Chairman*, Geo. L. Coyle, F. B. Dains. L. C. Newell, Edgar F. Smith

Honorary Membership: (Est. 1926) Marston T. Bogert, Columbia University, New York City, *Chairman*, Roger Adams, John Johnston, A. D. Little, Julius Stieglitz.

Industrial Alcohol: (Est. 1921.) Martin H. Ittner, Colgate & Company, Jersey City, N. J., *Chairman*, R. F. Bacon, J. H. Beal, E. H. Killheffer, Edward Mallinckrodt, Jr., R. H. McKee, H. W. Rhodehamel, Frederic Rosengarten.

Institute for Chemo-Medical Research: (Est. 1919.) Chas. H. Herty, Room 343, 1 Madison Ave., New York City, *Chairman*, J. J. Abel, C. L. Alsberg, R. F. Bacon, F. R. Eldred, Reid Hunt, T. B. Johnson, Julius Stieglitz, F. O. Taylor.

Journal of Physical Chemistry. A. C. S. Representatives on Editorial Board: (Est. 1924.) A. L. Day, G. A. Hulett, Irving Langmuir, W. Lash Miller.

Membership. (Est. 1876.) W. D. Bigelow, National Canners' Assoc., 1739 H St., N. W., Washington, D. C., *Chairman*, F. G. Cottrell, Chas. L. Parsons.

Metric System: To coöperate with the American Metric Assn., World Trade Club, London and Manchester Metric Association: (Est. 1915.) E. C. Bingham, Lafayette College, Easton, Pa., *Chairman*, Wm. Blum, W. F. Coover, E. W. Magruder, W. A. Noyes, Wm. Segerblom, R. E. Swain,

National Research Council Representatives from A. C. S. Term expires 1927: L. H. Baekeland, M. T. Bogert, E. W. Washburn: *Terms expire 1928:* Geo. L. Coyle. Wm. McPherson, H. S. Taylor; *Terms expire 1929:* H. N. Holmes, S. C. Lind, C. L. Parsons.

Nomenclature, Spelling and Pronunciation: (Est. 1894.) E. J. Crane, Editor, *Chemical Abstracts*, Ohio State Univ., Columbus, Ohio, *Chairman*, Board of Editors of the *Journal of the American Chemical Society*, Editor of *Industrial and Engineering Chemistry*, and A. M. Patterson.

Occupational Diseases in Chemical Trades: (Est. 1913.) L. W. Fetzer, 1428 Washington Ave. Dallas, Tex., *Chairman*, Geo. P. Adamson, Edward Bartow, H. K. Benson, M. L. Crossley, H. H Dow, F. R. Eldred, Elias Elvove, E K. Strachan, A. H. White.

Paper: (Est. 1908.) F. P. Veitch, Bureau of Chemistry, Washington, D. C.

Patent and Related Legislation: (Est. 1899.) Henry Howard, Grasselli Chemical Company, Cleveland, Ohio, *Chairman*, E. A. Hill, H. C. Parmelee, W. A. Schmidt, C. P. Townsend.

Preparation and Publication of a List of Ring Systems Used in Organic Chemistry. Joint with the National Research Council: (Est. 1922.) A. M. Patterson, Xenia, O., *Chairman*, M. T. Bogert, J. W. Kinsman, W. A. Noyes, R. R. Renshaw.

Prize Essays: H. E. Howe, Mills Bldg., Washington, D. C., *Chairman*, W. D. Bancroft, Chas. H. Herty, Paul Smith.

Revision of Methods of Coal Sampling and Analysis (Joint with the Society for Testing Materials): (Est. 1912.) S. W. Parr, Urbana, Ill., *Chairman*, A. C. Fieldner, A. H. White.

Standard Apparatus: (Est. 1917.) W. D. Collins, U. S. Geological Survey, Washington, D. C., *Chairman*, W. A. Boughton, H. E. Howe, F. W. Smither, G. C. Spencer, H. H. Willard.

Standard Methods for the Examination of Water and Sewage to Coöperate with Committee of American Public Health Association: (Est. 1920.) Arthur M. Buswell, Univ. of Ill., Urbana, Ill., *Chairman*, W. D. Collins, F. W. Mohlman, E. B. Phelps.

Standardization of Biological Stains: (Est. 1924.) A. C. S. Representative, Joseph A. Ambler, Peil Hotel, St. Petersburg, Fla., *Chairman*

Standardized Methods for Vitamin Research: (Est. 1921.) H. C. Sherman, Columbia University, New York City, *Chairman*, A. D. Emmett, A. F. Hess, E. V. McCollum, L B. Mendel.

Supervision of Chemical Engineering Catalog: (Est. 1915.) Wm. Hoskins, Room 2009, 111 W. Monroe St., Chicago, Ill.

Supervisory on Standard Methods of Analysis: (Est. 1910.) H. H. Willard, University of Michigan, Ann Arbor, Mich., *Chairman*, A. C. Langmuir, G. E. F. Lundell, W. W. Skinner, G. C. Stone.

Issued with the September Number, 1926

Proceedings

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MEMBERS ELECTED BETWEEN JUNE 15 AND AUGUST 15, 1926

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Gastron, S. M.

Akron Section
Manchester, Frank H.
Szegvari, A.

California Section
Glade, H. A.
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Philip, W. B.
Roper, E. E.
Strain, H. H.
Woodward, T.

Central Texas Section
Brockschmidt, C. L.

Chicago Section
Johnson, F. W.
Parks, C. T.
Phares, W. C.

Cincinnati Section
Wohrman, C. R.

Cleveland Section
Beck, E.
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Tucker, C. M.

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Welek, F. M.

Columbus Section
Beasley, Hershal V.
Clippinger, D. R.
Darling, F. S.

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Myers, R. P.
Reynolds, H. D.
Stark, C. N.

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Mohler, A. L.

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Nelson, W.

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Law, G. H.

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Adeline, Sister M.

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Miller, W. S.
Purdy, Daisy
Traxler, R. N.
Zieske, V. W.

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Jones, Margaret H.

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Beadle, Harold I.
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McKeen, J. E.

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Mason, C. W.

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Brieyer, Michael
Brooks, H.
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Schurch, C. F.
Talbert, E. J.

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Meyer, E.
O'Neill, G. D.

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Johnson, A. G.

Oklahoma Section
Robertson, H. J.

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Johnson, E., Jr.
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Lieber, E. D.
Molony, S. B.
Wells, R. L.

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Puget Sound Section

Tomkins, W. M.

Rhode Island Section

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Kennedy, R.
Marcaccio, W.

Rochester Section

Miriam, Sister R.

Savannah Section

Harris, H. L.

St. Louis Section

Alton Barium Products Co.
Lillieqvist, G. A.

Southern California Section

Banks, S. A.
Prescott, C. H , Jr.
Woelflin, Wm.

Wisconsin Section

Fosbinder, R. J.
Gehrand, C. E.

No Section

Abramson, H. A.
Attwood, A. J.
Bayley, H. W.
Chikamori, S.
Colon, E. D.
Dahlquist, G. H.
Dearsley, W. L. M.
Dick, R.
Doherty, C. H., Jr.
Griffiths, M. E.
Groth, B. S
Harrison, L. B.
Itomi, H.
Jones, W.
Kawanami, H.
Kinishita, Y.
Kubo, R.
MacDonald & MacDonald
Motoni, N.
Muzzy, M. F.
Nomura, T.
Ohara, E.
Ohashi, Y.
Osada, T.
Peard, W. L.
Sandera, K.
Swanberg, C.
Takata, T.
Walker, W. G.

DECEASED

Anderson, J. Arthur, 4346 N Keeler Ave , Chicago, Ill. Died.
Carter, Carnie Blake, Mellon Institute, Pittsburgh, Pa. Died, June 16, 1926.
Davidson, Herbert F., 152 Bayard St., Providence, R. I. Died, April 28, 1926.
Doolittle, R. E., 2217 Grant St , Evanston, Ill Died, April 25, 1926.
Flachslaender, Joseph, 708 West 26th St., Wilmington, Del. Died, April 28, 1926
Grotta, Bennett, 107 East Broad St., Tamaqua, Pa. Died.
Heinemann, Arthur, Victoria and Station Hotel, Preston, England. Died, April 5, 1926
Kahn, Max, Beth Israel Hospital, 70 Jefferson St., New York City. Died, April 8, 1926
Lyons, A. B., 274 Alger Ave., Detroit, Mich. Died, April 13, 1926.
Moore, Philip A., 7 Parkland Place, St. Louis, Mo. Died, May 15, 1926.
Morrow, C. A , Dept. of Agri., University Farm, St. Paul, Minn. Died, July 1, 1926.
Nyman, Ernest, 233 Fort St , Winnipeg, Man., Canada. Died, June 2, 1926
Quimby, Harold W., 83 Tacoma St., Rochester, N Y. Died, June 15, 1926.
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THE EFFECT OF MOISTURE AND PARAFFIN SURFACE ON THE RATE OF REACTION OF NITRIC OXIDE AND OXYGEN

By R. Leonard Hasche[1]

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In a previous investigation,[2] the effect of increased glass surface on the velocity of the reaction between nitric oxide and oxygen was studied. It appeared that this rapid reaction is not greatly affected by surface; that it takes place chiefly in the gas phase. When we consider that the rate of the reaction which we measure is the sum of the rates by different paths, altering the kind or amount of surface may be supplying or removing a catalyst. Accordingly, the net speed may be altered by introducing or eliminating paths through which the reaction may proceed. As possibilities of catalysts in the present case we may consider nitrogen tetroxide or moisture. Cohn and Jung[3] have recently shown in their study of the photochemical union of chlorine and hydrogen that with a pressure of water vapor under 10^{-7} mm. of mercury, no combination occurs; at a pressure of 10^{-5} mm., 88% is converted and at 10^{-3} mm. maximum catalysis results. This means that in case a film of moisture on a surface acts as a catalyst, only a very low moisture content, perhaps a monomolecular layer, is necessary to produce the maximum effect. More recently Norrish[4] has calculated from the description of the apparatus used in the experiments of Cohn and Jung that at a pressure of 10^{-3} mm. of mercury the monomolecular layer on the surface of the reaction vessel was just complete. Bodenstein and Dux[5] also found that evacuation to 10^{-3} mm.

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[1] National Research Fellow in Chemistry.

[2] Patrick and Hasche, This Journal, 47, 1207 (1925).

[3] Cohn and Jung, *Z. physik. Chem.*, 110, 705 (1924).

[4] Norrish, in a paper presented at the general discussion on photochemical reactions in liquids and gases, held by the Faraday Society at Oxford, October 1st and 2nd, 1925.

[5] Bodenstein and Dux, *Z. physik. Chem.*, 85, 297 (1913).

produced no effect on the speed of photochemical union of chlorine and hydrogen. In the event of a reaction product forming an adsorbed film which acts as a catalyst, the first experiment made with a fresh surface should show a different rate or trend than do succeeding experiments, since the adsorbed film is not removed by customary pumping. Too often the first experiment is a failure or we may ascribe its non-agreement with succeeding experiments to some unknown source of error.

In the present work an attempt was made to determine the effect of a paraffin-coated reaction chamber and of moisture, sulfur dioxide and nitrogen tetroxide on the speed of reaction of nitric oxide and oxygen at 25°.

Experimental Part

The apparatus and procedure were similar to those used in the previous work with the following exceptions. A single stopcock with a double-bore key replaced the two stopcocks which connected the storage bulbs with the reaction vessel. The apparatus was made entirely of Pyrex glass. A liquid-air trap was inserted in the vacuum line and pumping was done by a mercury diffusion pump backed by a Nelson oil pump. Evacuation was carried down to a pressure of 10^{-4} mm. of mercury. The gases remained in contact with phosphorus pentoxide for two months before being used in the experiments.

A great many experiments were made and it was found that the results were easily reproducible. Therefore, only one table of experiments made under a given set of conditions is included. Table I shows the results obtained with a Pyrex glass reaction chamber which was flamed during evacuation; evacuation was carried down to the pressure stated above. It will be noted that no reaction occurred during the first ten seconds as indicated by the manometer readings. This induction period appeared in all of the experiments performed at these low pressures with the exception of those experiments made with water vapor in the reaction chamber. In the earlier work, higher pressures of the reacting gases were used and the above phenomenon was not observed. Table II shows the results of an experiment made under the same conditions that obtained with Table I

TABLE I

EXPERIMENT 25

$a = 105.2; b = 74.1$

T''	$\Sigma\Delta_p$	α	x	dp/dt	$k\times10^{-7}$	T''	$\Sigma\Delta_p$	α	x	dp/dt	$k\times10^{-7}$
5	0	...	...	...	..	160	12.4	0.955	11.9	0.115	4.87
10	0	...	...	...	..	200	14.4	.949	13.7	.097	4.86
25	1.8	0.997	1.8	0.236	4.59	240	16.3	.942	15.4	.076	4.70
40	3.2	.990	3.2	.218	4.66	280	17.8	.937	16.8	.067	4.62
60	5.3	.979	5.2	.189	4.66	340	19.6	.932	18.4	.058	4.80
90	7.8	.971	7.6	.160	4.72	400	21.3	.927	19.9	.047	4.68
120	10.0	.963	9.6	.130	4.51	480	23.0	.922	21.3	.038	4.54
										Av.	4.69±0.08

but with initial partial pressures of the same magnitude that was used in the preceding investigation; it is seen that no induction period occurs although the velocity coefficients are identical with those of Table I. The induction period will be discussed at greater length later in the paper.

TABLE II

EXPERIMENT 2

$a = 172.5$; $b = 183.0$

T''	$\Sigma\Delta_p$	α	x	dp/dt	$k \times 10^{-7}$	T''	$\Sigma\Delta_p$	α	x	dp/dt	$k \times 10^{-7}$
10	12.0	0.956	11.5	2.076	5.03	90	55.3	0.850	48.1	0.430	4.59
15	18.2	.936	17.1	1.750	5.09	110	60.4	.841	52.1	.350	4.68
20	22.6	.923	21.0	1.416	4.70	130	64.4	.834	55.2	.282	4.56
25	26.3	.913	24.2	1.280	4.76	150	67.8	.829	57.9	.244	4.58
35	33.0	.895	29.9	1.010	4.67	180	71.8	.822	60.9	.195	4.66
45	38.9	.882	34.8	0.830	4.69	210	75.0	.817	63.4	.156	4.53
55	43.5	.873	38.6	.700	4.67	240	77.9	.813	65.6	.130	4.53
73	51.0	.858	44.7	.513	4.60	280	80.8	.809	67.9	...	..
											Av. 4.69 ± 0.11

Expt. 7 was made with a paraffin-coated reaction chamber; it indicates that the speed of the reaction has been reduced over 20% as compared with the two preceding experiments. There is a marked trend in the velocity coefficients to lower values after the first minute and then a return to the initial value as the reaction proceeds to completion, which is slightly greater than the experimental error. In another experiment, not included in the paper, the lower value of the velocity constants was maintained to the end of the reaction. The paraffin coating used in these experiments was about 1 mm. in thickness. In other experiments, thin coatings of paraffin as well as paraffin oil coatings failed to show any difference in the speed of the reaction as compared with that in uncovered reaction vessels. The surface of the glass apparently was not covered; inspection showed that the thin coating of solid paraffin was badly cracked and crystalline, and in some places was raised from the surface of the glass, probably due to evaporation of some lighter constituents during evacuation.

TABLE III

EXPERIMENT 7

$a = 142.7$; $b = 128.0$

T''	$\Sigma\Delta_p$	α	x	dp/dt	$k \times 10^{-7}$	T''	$\Sigma\Delta_p$	α	x	dp/dt	$k \times 10^{-7}$
5	..	...	..	...	..	95	24.5	0.918	22.7	0.285	3.48
10	..	...	..	...	..	130	29.1	.906	26.6	.212	3.27
15	4.0	0.983	4.0	0.750	3.67	160	32.0	.898	29.0	.176	3.18
20	6.2	.975	6.1	.700	3.82	190	35.4	.890	31.9	.147	3.22
30	9.8	.963	9.5	.620	3.92	220	37.9	.885	34.0	.130	3.32
40	12.9	.953	12.3	.535	3.83	250	40.2	.880	35.9	.122	3.49
50	15.8	.943	14.9	.460	3.73	280	42.0	.876	37.4	.111	3.69
70	20.7	.930	18.9	.360	3.58	340	44.7	.870	39.6	.094	3.83
											Av. 3.58 ± 0.21

A shellac coating was also tried but apparently it was attacked by the oxides of nitrogen as the reaction followed a second-order law more closely than that of the third order. It should be pointed out that the glass surface was not completely covered with paraffin as it was impracticable to coat the connecting tubes and capillaries.

Expt. 27 (Table IV) was made in the presence of 44.0 mm. of sulfur dioxide. The velocity coefficients showed no trend and are slightly less than those of Expts. 25 and 2, but we are probably not justified in saying that sulfur dioxide has a real effect, since the difference is so small. The experiment is in accord with the idea commonly held that sulfur dioxide and the oxides of nitrogen do not react in the absence of moisture.

TABLE IV

Expt.	Conditions of experiment	Evacuation to	Speed at zero time	Initial press. of reactants		Induction period	Av. velocity constant $\times 10^{-7}$	Av. deviation
				$a(O_2)$	$C(NO)$			
25	Glass	10^{-4}[a]	1	105.2	74.1	Present	4.69	0.08
2	Glass	10^{-4}[a]	10	172.5	183.0	None	4.69	.11
7	Paraffin	10^{-4}[a]	4	142.7	128.0	Present	3.58	.21
27	Sulfur dioxide in glass	10^{-4}[a]	2.6	102.3	122.3	Present	4.44	.08
36	Nitrogen tetroxide in glass	10^{-4}[a]	1.9	98.7	105.0	Present	4.93	.19
26	Water for 48 hours	10^{-4}[a]	1.7	115.5	91.0	None	5.16	.06
20	Glass in equilibrium with air	10^{-3}	1	78.1	86.2	Present	5.25	.04

[a] Liquid-air trap used.

Expt. 36 (Table IV) shows that the reaction product has little effect on the speed of union of nitric oxide and oxygen under the present conditions; the velocity constants showed no trend and are only slightly increased over those of Expts. 25 and 2. Nor should we expect catalysis by $N_2O_4 \rightleftharpoons 2NO_2$, since the velocity coefficients are constant throughout, which would not be true in the case of an autocatalytic reaction. Some of the reaction product of the previous experiment supplied the equilibrium mixture of the dioxide and tetroxide for the present experiment. Since time was allowed for the reaction to have gone to completion, the fraction of the total pressure which was oxygen (all experiments were carried out with an excess of oxygen) could be calculated and this, subtracted from the total pressure as registered by the α-bromonaphthalene manometer, gave 29.1 mm. of the equilibrium mixture. This corresponds to a pressure of 15 mm. of nitrogen tetroxide calculated as undissociated.

In the calculation of this experiment, correction for the dissociation of N_2O_4 is as follows. All pressures are expressed in millimeters of α-bromonaphthalene at 25°. The decrease in pressure, $\Sigma\Delta_p$, is related to the pressure of nitric oxide and oxygen reacting by the expression $\Sigma\Delta_p = P(\alpha - \alpha_1) + x(\alpha - 2)$, in which P is the pressure of nitrogen tetroxide present at zero time calculated as undissociated, x is one-half the pressure of the nitric oxide that has reacted, α is the degree of dissociation of $(P + x)$ mm. of tetroxide, or the total amount present at any time interval, and α_1 is the degree of dissociation of tetroxide present at zero time. A curve was drawn showing the relation between the pressure of the tetroxide and its degree of dissociation. The values for this curve were obtained by substituting in the expression $K_p = 4P^2/(1-\alpha)$. Another curve gave the relation between $\Sigma\Delta_p$ and x for a given total pressure of tetroxide of P as given above. The value of K_p used here and in all of the experiments is 0.134; it was calculated from the work of Bodenstein and Linder[6] for a temperature of 25°. The velocity coefficients are instantaneous rate constants, the values dp/dt being read from the curve by the mirror method.

The effect of water vapor is shown in Expt. 26 (Table IV). The apparatus was evacuated as usual; water vapor was then admitted through a stopcock from a small bulb containing water. This bulb had previously been sealed into the apparatus, frozen out and evacuated. Both the storage bulbs and the reaction vessel were opened to the same pressure of water vapor. Immediately after the stopcock to the bulb containing liquid water had been closed, a reading was taken on the α-bromonaphthalene manometer which gave a pressure of 3.5 mm. The large, four-way stopcock between the storage bulbs and reaction vessel was now closed and the former were filled with a supply of the respective gases, nitric oxide and oxygen. The system, including gases in the storage chambers, now stood in contact with the water vapor for 48 hours before the experiment was performed. At the end of that time the pressure of water vapor had fallen to 1 mm. of α-bromonaphthalene. The velocity constants show no trend and no induction period; their average was about 10% greater than those of Expts. 25 and 2.

Orientation experiments were now made of which Expt. 20 (Table IV) is one. The apparatus was opened to the atmosphere for some time and then pumped down to a pressure of 10^{-3} mm. of mercury, omitting the liquid-air trap. The results check well with the preceding one showing, however, an induction period during the first ten seconds.

Discussion of Results

The results of the experiments cited are collected in Table IV. In Col. 4 the relative speeds of the reactions at zero time are calculated from the initial pressures of the reactants. It is apparent that the induction period is a function of the initial pressures and is also influenced by the moisture content of the system. We cannot be certain that there is no induction period in Expts. 2 and 26; however, if it does occur, it must be of short duration. There is an uncertainty of one second in zero time and a maximum error of 1.5–2.5 mm. of α-bromonaphthalene (depending upon the pressure) in the calculation of the initial pressures from the photographic

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[6] Bodenstein and Linder, *Z. physik. Chem.*, **100**, 87 (1922).

films. A study of Table IV reveals that the induction period cannot be of purely thermal origin, analogous to the Draper effect, nor can it be ascribed to a lag in the manometer liquid, as inspection of Expts. 7, 27, 36 and 26 will show. Two other explanations are possible: (1) the induction period may represent the time necessary to destroy an inhibitor of the reaction, such as in the case given by Burgess and Chapman,[7] where ammonia was found to inhibit the union of chlorine and hydrogen; or (2) we may assume that a primary process is taking place in this apparent halting period. We are not able, from the experimental evidence obtained in this investigation, to decide between the two possibilities. Recently, Weigert and Kellermann[8] have found some support for the occurrence of a primary process. They studied by a photographic method the early part of the reaction between chlorine and hydrogen. The study indicated the formation of a fog within the first fiftieth of a second and its disappearance after an equal period; a purely chemical reaction then followed. It appears probable that a gas reaction of this sort is composed of a chain of consecutive reactions and that water has an important part in such a mechanism.

A mechanism for the role of water in this reaction might be the formation of $NO\text{-}H_2O$ and of $(NO)_2\text{-}H_2O$. The latter aggregate on collision with an oxygen molecule could form the product according to the scheme:

$$NO + H_2O = NO\text{-}H_2O$$
$$NO\text{-}H_2O + NO = (NO)_2\text{-}H_2O$$
$$(NO)_2\text{-}H_2O + O_2 = N_2O_4 \rightleftharpoons NO_2 + H_2O$$

The present work furnishes evidence that there is a chemical catalysis produced by moisture. Baker has shown that the "super-dried" gases nitric oxide and oxygen do not react. The paraffin surface and other conditions imposed in the present experiments would then serve only to alter the moisture content. In the ordinary evacuation a film of moisture several molecules deep occurs and maximum catalysis has undoubtedly been reached. The experiments of d'Huart[9] show that after the usual evacuation in the presence of phosphorus pentoxide 0.009 mg. of water per sq. cm. of glass surface remains adsorbed. The number of molecular layers, Θ, may be calculated from the formula $\Theta = gN\sigma^2/M$, in which g is the weight of water adsorbed per sq. cm. of glass surface, N is the Avogadro number, M is the molecular weight of water and σ the diameter of the molecules calculated from the kinetic theory. If we take the value of 2.6×10^{-8} for σ,[10] then $\Theta = 20.5$. This we may compare with the value $\Theta = 51.8$ given by McHaffie and Lenher[11] for the moisture film in equi-

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[7] Burgess and Chapman, *J. Chem. Soc.*, **89**, 1399 (1906).

[8] Weigert and Kellermann, *Z. physik. Chem.*, **107**, 1 (1923).

[9] d'Huart, *Compt. rend.*, **180**, 1594 (1925).

[10] See Landolt-Börnstein-Scheele-Roth, "Tabellen," 5th edition.

[11] McHaffie and Lenher, *J. Chem. Soc.*, **127**, 1559 (1925).

librium with liquid at 25°. At about 40°, according to the same authors, the water film is less than one molecule deep, so it is safe to assume in the experiments made under the conditions of Expts. 25, 2, 7, 27 and 36, that there was a very small moisture content, less than a monomolecular layer. The above considerations emphasize our meager knowledge of the mechanism of gaseous reactions. The study of the oxidation of nitric oxide at lower pressures will be continued by means of a motion-picture camera in order to gain some insight in regard to the induction period.

Summary

1. Moisture catalyzes the reaction between nitric oxide and oxygen. The decrease in velocity with a paraffin surface has been interpreted as due to a decreased amount of moisture. Water vapor produces a maximum increase of speed of 50% over that in a paraffin-lined vessel.

2. Sulfur dioxide and the reaction product have practically no effect on the speed of reaction.

3. An induction period with a duration of ten seconds has been noted at initial partial pressures of the gases below about 14 mm. of mercury.

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[Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 181]

THE UNIMOLECULARITY OF THE INVERSION PROCESS

By George Scatchard

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If the rate of a reaction be defined as that fraction of a reactant present in the system which reacts in unit time, this definition may be expressed mathematically as

$$R = \frac{-\mathrm{d}y/y}{\mathrm{d}t} = \frac{-\mathrm{d}\,ln\,y}{\mathrm{d}t} \tag{1}$$

in which R is the rate, t is the time and y is the quantity of the reactant in the system at the time t. Since y occurs in a ratio or in a logarithm, it may be expressed in any units—as mass, as moles or, corresponding to the quantity actually measured in most inversion experiments, as $\lambda - \lambda_\infty$, where λ is the optical rotation in a tube of any definite length, and the subscript ∞ refers to complete inversion. It is somewhat more convenient to work with another quantity, r, defined by the equation

$$r = 0.4343\,R = \frac{-\mathrm{d}\log y}{\mathrm{d}t} \tag{2}$$

It is customary, for unimolecular reactions, to assume that the rate as defined above is constant and to integrate Equations 1 or 2 to determine the numerical value of the rate. However, the very accurate measurements of Pennycuick[1] indicate that the rate of inversion of sucrose increases slightly during the course of the reaction. Therefore, the classical integrated expression should not be applied to these measurements, and Equation 2 cannot be integrated unless r be known as a function of t.

The rate at any time may be obtained by determining the slope of a smooth curve through the points obtained by plotting $-\log y$ against t. The accuracy of this method may be very considerably increased by plotting $-At-\log y$ against t, in which case r is A plus the slope of the curve. A is most conveniently chosen as $(-\log y)/t$ for the last measurement. For Pennycuick's measurements in the more dilute solutions the time interval is so large that even this method is less accurate than the precision of the experimental work warrants. In such a case $-At - \log y$ may be plotted against $\sqrt{t}$, and the slope of the curve so obtained divided by $2\sqrt{t}$ added to A to give r [since $\mathrm{d}x/\mathrm{d}t = (\mathrm{d}x/\mathrm{d}\sqrt{t})(\mathrm{d}\sqrt{t}/\mathrm{d}t) = (\mathrm{d}x/\mathrm{d}\sqrt{t})/(2\sqrt{t})$].

TABLE I

CHANGE OF REACTION RATE WITH FRACTION INVERTED

	0.02 N HCl[a]	0.099 N HCl	0.507 N HCl	0 905 N HCl
	40°	35°	35°	35°
k =	0 000605	0 001629	0.01045	0.02301
Fraction inverted	r/k	r/k	r/k	r/k
0.05	0.982	0.974	0.962	....
.10	.989	.978	.967	0.966
.20	.995	.984	.971	.969
.30	.998	.987	.975	.972
.40	1.000	.990	.978	.973
.50	1.000	.995	.981	.974
.60	1.000	.999	.983	.976
.70	1.000	1.000	.985	.979
.80	1 000	1.000	.986	.980
.90	1.000	1 000	.988	(0.978)

[a] In each case the concentration of sucrose is 171 g. per liter.

In Table I are given the rates obtained by applying this method to the measurements of Pennycuick divided by appropriate constants, k, for certain fractions of sucrose inverted. With 0.92 N acid the rate is constant within 0.1% after the sucrose is 35% inverted; with 0.099 N acid a constant value is not reached until 60% is inverted; the rate with 0.507 N acid increases continually; and the rate with 0.905 N acid passes through a maximum at 80% inversion. This last phenomenon is probably due to a small error in the determination of the rotation at complete inversion caused by side reactions in the presence of the strong acid. The rates in 0.907 N acid after 80% inversion are enclosed in parentheses, and are disregarded in the discussion that follows.

Table II contains the same ratios as Table I, but for definite time in-

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[1] Pennycuick, THIS JOURNAL, 48, 6 (1926).

TABLE II

CHANGE OF REACTION RATE WITH TIME

Time, minutes	0 02 *N* HCl r/k	0.099 *N* HCl r/k	0 507 *N* HCl r/k	0 905 *N* HCl r/k	Eq. 3 r/k
5	....	0.969	0 967	0.971	0.971
10	. ..	.973	.971	.973	.973
20	0.974	.975	.976	.976	975
30	.978	.978	.981	.980	978
40	982	981	.983	(0.978)	980
60	.987	.984	.986	(0.976)	984
80	.989	.986	.986	....	.987
100	.992	.988	.988		.989
150	.994	.992	....		.993
200	.996	.996			.996
300	.999	1.000			.998
400 to end	1.000	1.000			1.000

tervals after the start of the reaction. The last column contains the ratio calculated by the equation

$$r = k(1 - 0.03\, e^{-0.01t}) \tag{3}$$

The form of Equation 3 and the values of the numerical constants were obtained empirically from the results for the two solutions more dilute in acid, for which the values of k must be the final values of r. Then Equation 3 was used to determine k for the two more concentrated solutions. The agreement is very good. The maximum deviation of the measured rates from those calculated is 0.4%, and the average deviation is 0.13%. A comparison of the two tables shows clearly that the rate is a function, not of the fraction inverted, but of the time.

Combining Equations 2 and 3, we may integrate between the time limits 0 and t, or between t_1 and t_2, to obtain

$$\log \frac{y_0}{y} = k[t - 3(1 - e^{-0.01t})] = kt\left[1 - \frac{3}{t}(1 - e^{-0.01t})\right] \tag{4}$$

$$\begin{aligned} \log \frac{y_1}{y_2} &= k[t_2 - t_1 - 3(e^{-0.01t_1} - e^{-0.01t_2})] \\ &= k(t_2 - t_1)\left[1 - \frac{3}{t_2 - t_1}(e^{-0.01t_1} - e^{-0.01t_2})\right] \end{aligned} \tag{5}$$

These expressions divided by t or by (t_2-t_1) correspond to the classical "specific reaction rate" or "velocity constant." Equation 4 may be compared with the experimental measurements independently of the graphic determination of the slopes. The mean deviations of the average "constants" from those computed by Equation 4 are for the four series: 0.5, 0.3, 1.2 and 0.8%, but the deviations for very short time intervals indicate a constant time error. If the average values be corrected by subtracting from the times the quantities: 0.2, 0.0, 0.1, 0.05 minutes, the mean deviations become: 0.3, 0.3, 0.4, 0.4%, without any trend with time. For the first two series the mean deviation of the individual measurements from their averages is 0.2 and 0.5%, so the agreement with the theory is as good as could be expected, and the time correction does not attribute an unreasonable error to the determination of the time of a reaction started by pouring one solution into another and stopped by pouring through a cooling coil.

From the nature of the change in rate it is possible to draw several conclusions as to the cause of the change. In the graphical method the start of the reaction is treated as any other point on the curve, and any error in the initial rotation or in the time of starting the reaction is completely eliminated after the first few measurements. For the same reason a constant time error, due to the reaction continuing a little during the cooling, would also be without effect. The time error indicated by the integrated Equation 4 is discussed above. There can be no significant error in the final rotation, except for the values enclosed in parentheses, for such an error would give a more rapid change toward the end of the reaction. Lack of thermal equilibrium because of heat produced or absorbed during the reaction would give a larger effect for the more rapid reactions and is therefore excluded.

The increase in rate cannot be caused by a change in the environment as the concentration of sucrose decreases and that of inert sugar increases, for such a change would persist throughout the reaction and would be nearly independent of the acid concentration. Table I shows clearly that the change in reaction rate fulfils neither of these criteria.

Equation 3 may be explained by the attainment of equilibrium in a process originally somewhat displaced from equilibrium for which the rate of attaining equilibrium is proportional to the displacement. This is more clearly shown in the differential form

$$dr/dt = 0.01\ (k - r) \tag{6}$$

Two causes for such a change suggest themselves. The temperature of the solution might be lower than that of the thermostat at the start of the reaction. This explanation would demand that the temperature be 0.2–0.3° too low after 40 minutes in the thermostat, and that five hours be required to attain thermal equilibrium. It is, therefore, highly improbable. The mixing of the solutions might not be quite complete at the start, and true homogeneity might be attained only by diffusion. Five hours does not appear too long for this process, and it seems very probable that pouring the solutions from one flask to another does not result in absolutely complete mixing. It may be concluded that Equations 3 to 6 are characteristic of the technique of Pennycuick but not of the inversion process, and that the rates of inversion do not change more than a few tenths of a per cent. during the course of the reaction. The most probable values of the rates are the k's given in Table I, even for the cases where the measured rates never attain these values.

In the paper of Pennycuick the results are expressed by the classical "reaction velocity," which may be shown from Equations 3 and 4 to change more uniformly than the rate, and the conclusion is reached that the change is due to increasing activity coefficients of the hydrogen ion and of the sucrose. It has been shown above that the present more precise treatment makes these conclusions untenable. The evidence for the increase in the hydrogen-ion activity appears sound, but these results indicate that there must be some compensating tendency to diminish the rate. It is much less certain that the activity coefficient of the sucrose increases during the inversion. The point of view of Pennycuick's paper is very similar to that presented by Moran and Lewis[2] except that other factors considered in the earlier paper are not discussed in the more recent one. This point of view has been criticized in detail in earlier papers.[3]

Summary

The precise measurements by Pennycuick of the rate of inversion of sucrose have been treated by a mathematical method more accurate than any hitherto applied to reaction rates. The rates have been determined graphically and an equation has been derived relating the change of rate to the time of reaction. From the nature of the change in rate it is shown that several possible experimental errors give no disturbance, and that the change cannot be due to a change in the environment but is most probably due to slightly inefficient mixing. It is concluded that in homogeneous solutions the rates of inversion are constants within a few parts per thousand, and the most probable values of these rates are given.

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[Contribution from the Chemistry Laboratory of the University of California]

SOME THERMODYNAMIC PROPERTIES OF ELECTROLYTES IN ACETIC ACID AND IN LIQUID AMMONIA

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The freezing-point lowerings and other colligative properties of non-aqueous solvents, interpreted on the basis of ideal-solution relationships, led to the idea that electrolytes exist in a large number of non-aqueous solvents as simple molecules in equilibrium with associated molecules and with a small number of the ions of the electrolyte. At different concentrations, variations in the value of the colligative properties from that demanded by the laws of ideal solutions, were attributed to a shift in the equilibrium between ions, simple molecules and polymerized molecules. That such equilibria exist and that variations in the number of each molecu-

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[2] Moran and Lewis, *J. Chem. Soc.*, **121**, 1613 (1922).

[3] Scatchard, This Journal, **43**, 2387, 2406 (1921); **45**, 1580 (1923).

[1] National Research Fellow.

lar species depend upon the concentration of the electrolyte, are postulates which seem beyond doubt. The marked non-ideality, however, of solutions of electrolytes in which any appreciable number of ions are present, particularly in solvents of low dielectric constants, renders almost valueless any deductions to be made solely on the basis of the simple relationships obtaining in solutions approaching the ideal. It is to be remembered that, in order for any colligative property to be a direct measure of the number or state of the solute particles, the free energy of the solution at a given temperature and pressure must depend solely on the mole fractions of the constituents, while for a solution of ions there is a considerable contribution from the attractions and repulsions of the ions. The purpose of the present paper is to determine how far the freezing-point lowerings of certain nonaqueous solvents containing dissolved electrolytes may be explained on the assumption of *practically complete* ionization and the Debye-Hückel[2] theory of inter-ionic attractions, and to indicate the method of calculation of the activity coefficients of the ions in the solvents considered.

In accord with the theory of Debye and Hückel, the freezing-point lowering of a solvent containing a dissolved electrolyte is related in the following way to the properties of the solvent, the properties of the electrolyte and the composition of the solution

$$1 - \frac{\Delta}{\nu \Delta_K} = w \frac{\epsilon^2}{6\,DkT} \sqrt{\frac{4\pi\epsilon^2}{DkT} \nu n}\; \sigma \qquad (1)$$

where Δ is the observed freezing-point depression, Δ_K the freezing-point depression produced by an equivalent amount of an ideal solute, ν the total number of ions to be obtained from a molecule of the electrolyte, w a valence factor (equal to unity for uni-univalent electrolytes), ϵ the elementary charge of electricity, D the dielectric constant of the pure solvent, k the Boltzmann constant, T the temperature, n the number of molecules of the electrolyte (as would be determined by chemical analysis) per cubic centimeter and σ a function defined as follows,

$$\sigma = \frac{3}{\kappa^3 a^3} \left[1 + \kappa a - \frac{1}{1 + \kappa a} - 2 \log (1 + \kappa a) \right]$$

where a is the mean effective radius of the ions in solution, and κ is defined by the following equation:

$$\kappa^2 = \frac{4\pi\epsilon^2}{DkT} \sum_i n_i z_i^2$$

The value of the mean activity coefficient of the ions, derivable from the above expression for the freezing-point lowering, is

$$\log_e f = \frac{-z_i^2 \epsilon^2 \kappa}{2\,DkT} \, \frac{1}{(1 + \kappa a)} \qquad (2)$$

where z_i is the valence of the ion being considered.

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[2] Debye and Huckel, *Physik. Z.*, **24**, 185 (1923); **25**, 97 (1924); **26**, 93 (1925).

Application to Very Dilute Solutions of Electrolytes in Acetic Acid

The typical strong electrolytes sufficiently soluble in acetic acid for the purpose of experimentation are lithium halides, sodium bromide and the acetates. Substitution of numerical values in Equation 1 yields $1-(\Delta/2\Delta_K) = j = 6.77\sqrt{2c}\,\sigma$, where c is the concentration of the electrolyte in moles per liter.

A series of freezing-point experiments with acetic acid containing several salts at low concentrations has been made. The apparatus consisted of a Dewar vessel of capacity approximately 1 liter, which fitted into a metal container provided with closely fitting cover. This arrangement permitted keeping the air in the apparatus practically free from water vapor, since the apparatus could be filled with air dried over phosphorus pentoxide. The temperature was measured by means of a large Beckmann thermometer, calibrated to 0.002°, and with the use of a telescope freezing temperatures could be determined to within 0.001°. Various amounts of a saturated stock solution of the salt in acetic acid were added to the solvent in equilibrium with its solid phase, and the freezing-point depressions thus measured. The contents of the Dewar vessel were stirred by a motor-driven paddle, the shaft of which was securely packed so as to give a connection practically gas-tight.

After the attainment of equilibrium the stirring was suspended and portions of the solution were withdrawn through an especially arranged pipet so constructed as to cause minimum contamination of the solution with water vapor. The solutions were analyzed for halide ion by titration with silver nitrate and potassium thiocyanate, ferric alum being used as an indicator. In the case of the solution containing acetate as solute, the acetate was converted to chloride, and the same procedure followed.

The acetic acid was prepared from the ordinary commercial 99% acetic acid. This was frozen and allowed to melt partially and the liquid poured off. This process was repeated until the acid froze at a constant tempera-

TABLE I

Lithium bromide		Sodium bromide		Sodium acetate	
m	j	m	j	m	j
0.00422	0 35	0.00489	0.47	0.00728	0.47
.00561	.34	.00613	.45	.0148	.54
.00714	.34	.00892	.40	.0215	.57
.00912	.37	.0126	.51	.0335	.568
.0118	.48	.0151	.48	.0502	.562
.0194	.481	.0184	.50	.0169	.563
.0272	.485	.0208	.50	.0770	.559
.0334	.479	.0242	.50	.0984	.555
.0409	.497			.1242	.552
0468	.498				
0540	.514				
.0651	.525				

ture of approximately 16.6°. The salts were thoroughly dried by passing air (which had previously been passed over phosphorus pentoxide) over them. Subsequent analysis showed their purity to be entirely sufficient for these experiments. The experimental results for lithium bromide, sodium bromide and sodium acetate are given in Table I. Under the columns headed m the concentrations of the salts are given in moles per 1000 g. of acetic acid, and in the columns following are the corresponding values of j.

The comparison of the experimental results with those calculated is given graphically in Figs. 1, 2 and 3. The solid curves in the figures represent the graph of the equation

$$j = 6.77\sqrt{2c}\,.\,\sigma \qquad (3)$$

where

$$\sigma = \frac{3}{x^3}\left[1 + x - \frac{1}{1+x} - 2\log(1+x)\right]$$

and

$$x = 0.677\sqrt{2c} \times 10^8 \times a$$

The mean effective radius of the ions of an electrolyte is represented by a, and is the only specific property for the various electrolytes in a given solvent. The value of a for lithium bromide (Fig. 1) is 7.1×10^{-8}, that for sodium bromide (Fig. 2) is 6.8×10^{-8}, that for sodium acetate (Fig. 3) is 6.2×10^{-8}. The values of a were found by taking one point from the experimental curves in the range of high concentrations, where the error in determining j is presumably least, and calculating the corresponding a by means of the equations above. The points in the figures, deviating most widely from the theoretical curves, represent a discrepancy between calculated and observed freezing-point lowerings of less than 0.004°. For example, in Fig. 3, the deviation of the point at the lowest concentration represents a deviation in the freezing-point depression of 0.0018°.

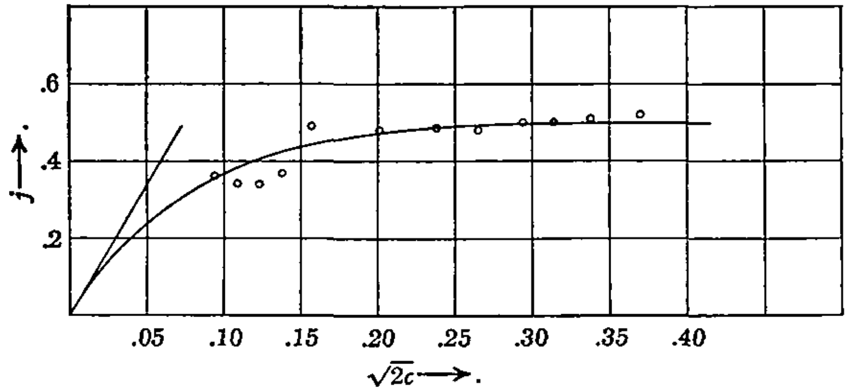

Fig. 1.—The relationship between j and the concentration of the solution for lithium bromide in acetic acid.

In so far as Equation 3 represents the experimental behavior of the freezing-point lowering by the presence of the electrolytes, the following equation may be used for the calculation of the mean activity coefficient of the ions.

$$\log_{10} f = \frac{-8.86\sqrt{2c}}{1 + 0.677\sqrt{2c} \times 10^8 \times a}$$

By means of this equation the activity coefficient of the ions of lithium bromide at a concentration of 0.00005 mole per liter is calculated to be 0.823, and at a concentration of 0.005 mole per liter to be 0.252.

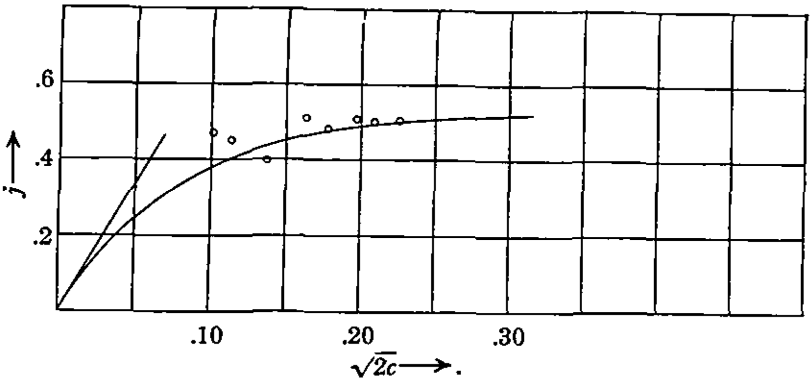

Fig. 2.—The relationship between j and the concentration of the solution for sodium bromide in acetic acid.

The Behavior of Electrolytes at Higher Concentrations in Acetic Acid

The general equation for j given above shows a slight maximum for j at values of the concentration depending upon the values of the constants entering the equation. For aqueous solutions and solutions of a similar type a maximum for j is the rule, beyond which maximum the values of j fall very rapidly with increasing concentration, much more rapidly than corresponds with the theoretical equation. In solutions of other types

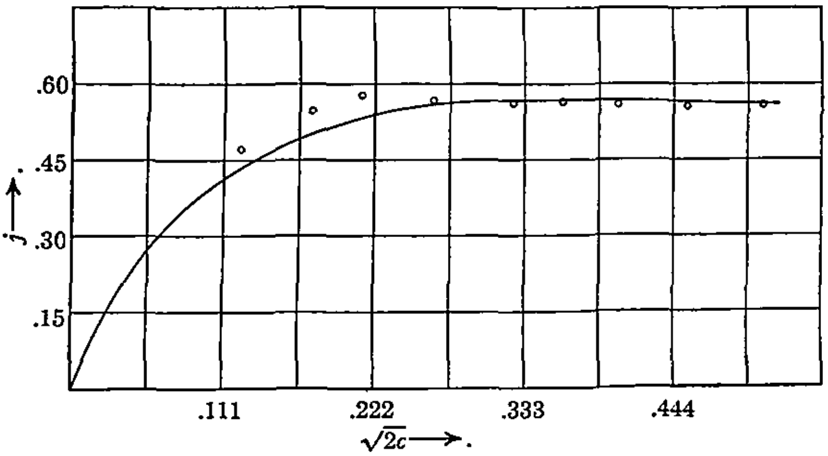

Fig. 3.—The relationship between j and the concentration of the solution for sodium acetate in acetic acid.

(acetic acid as solvent, for example) it is observed that j reaches a practically constant value, or continues to increase in value beyond the point corresponding with the maximum of the theoretical equation. Hückel[3] has considered the effects calculable for water solutions on the assumption that the dielectric constant of the solution is different from that of the pure solvent. On account of the electric fields arising from the ions, the solvent molecules in virtue of their electric moments will be oriented in the vicinity of the ion and will give rise to a sphere of solvent surrounding each ion not contributing its normal share to the polarization of the medium. This effect for aqueous solutions has been found experimentally by Walden, Ulich and Werner,[4] and calculated by Sack.[5]

In addition to the effect due to the orientation of the solvent molecules, the effect of adding to the solvent ions which are less polarizable than the solvent molecules tends to lower the dielectric constant. The phenomenon of electrostriction, however, increases the density of the solvent molecules in the vicinity of the ion and this effect, considered apart from saturation effects, would seem to result in an increase of the dielectric constant, but it is to be remembered that very near the ion where the increase of the density of the solvent is appreciable the polarization of the medium has already fallen almost to the value which corresponds with the optical polarizability of the medium.

Hückel, by considering that the dielectric constant decreases linearly with the increase of concentration of the ions, obtains the following equation for the activity coefficient of an ion in aqueous solution,

$$\log f = \frac{-z_1^2\epsilon^2\kappa}{2\,DkT}\,\frac{1}{(1+\kappa a)} + 2cK \qquad (4)$$

where K is a positive constant accounting for the changed dielectric properties of the solvent. The corresponding equation for j is

$$j = \frac{w\epsilon^2}{6\,DkT}\sqrt{\frac{4\pi\epsilon^2}{DkT}\nu n}\,.\,\sigma - cK \qquad (5)$$

The measurements made with lithium bromide, sodium bromide and sodium acetate were at concentrations too low to test Equation 5. A few measurements[6] have been made with lithium iodide and lithium nitrate, however, at high concentrations, which are of some importance for such a test. The data are given in Table II.

In the case of lithium iodide, if the values for j at the lower concentrations are used for the calculations of the constants a and K, they are found to be 6.75×10^{-8} and -1.38, respectively. The value for j at the highest concentration, as calculated from the resulting equation, is 0.725, as com-

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[3] Hückel, *Physik. Z.*, **26**, 93 (1925).

[4] Walden, Ulich and Werner, *Z. physik. Chem.*, **116**, 261 (1925).

[5] Sack, *Physik. Z.*, **27**, 7 (1926).

[6] Turner and Bissett, *J. Chem. Soc.*, **105**, [2] 1782 (1914).

pared with 0.710 found by experiment. In like manner for lithium nitrate, the constant a is found to be 7.17×10^{-8} and K to be —0.88. The value of j calculated for the highest concentration from the resulting equation is 0.650 as compared with 0.663 found by experiment.

TABLE II

THE FUNCTION j FOR ELECTROLYTES AT RELATIVELY HIGH CONCENTRATIONS IN ACETIC ACID

Lithium iodide		Lithium nitrate	
$\sqrt{2c}$	j	$\sqrt{2c}$	j
0.431	0.652	0.376	0.558
.496	.683	.540	.586
.579	.710	.689	.663

The agreement for these few values is considered fair, but the significance of the negative value of the constant K is not readily explained. If the electrolytes are practically completely ionized, almost every prediction to be made on a theoretical basis is that the dielectric constant is lowered by the presence of the ions, which fact in turn means that K is a positive quantity. The indication is that the electrolyte is not completely ionized in acetic acid. This viewpoint is to some extent confirmed by the experimental measurements of Walden and Ulich[7] of the dielectric constants of organic solvents containing dissolved electrolytes. In these measurements the dielectric constants of the solutions were found to be greater than those of the pure solvents. Whatever the real significance of the constants a

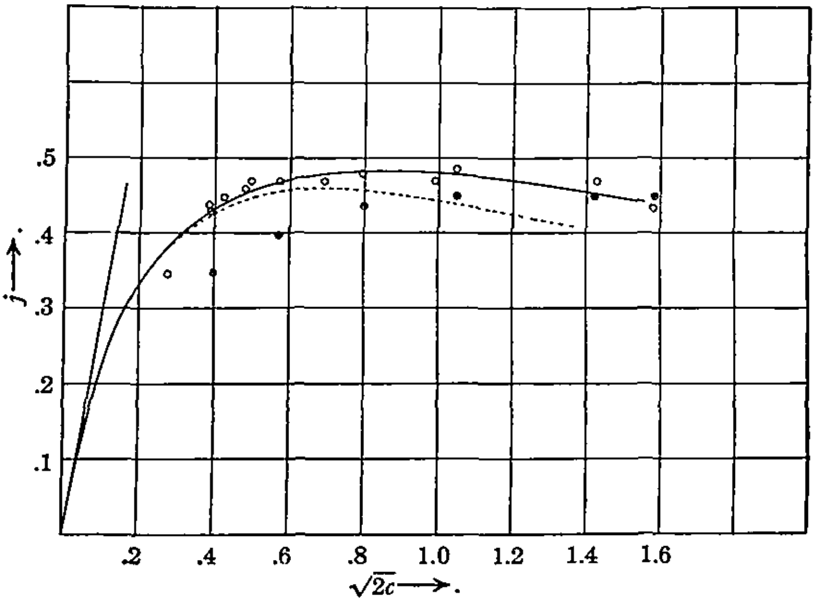

Fig. 4.—The relationship between j and the concentration of the solution for sodium nitrate in liquid ammonia.

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[7] Walden and Ulich, *Z. physik. Chem*, 110, 43 (1924).

and K, the effects of the dielectric constant and the concentration seem properly accounted for by the theory of Debye and Hückel; furthermore, the two-constant equation is obviously an extremely useful means of interpolation.

Application of the Theory to Solutions in Liquid Ammonia

The equation for j for uni-univalent electrolytes in liquid ammonia, in accord with the theory of Debye and Hückel, is

$$j = 2.862\sqrt{2c}\,\sigma - cK \qquad (6)$$

where the constant 2.862 depends upon the dielectric constant of liquid ammonia at its freezing point (25.1), the freezing temperature and certain universal constants, c is the concentration of the electrolyte in moles per liter, and σ is the function as defined above. In Fig. 4 are plotted the graph of Equation 6 (solid curve) and the experimental results found by Elliott[8] for sodium nitrate, as well as the graph of the equation $j = 2.862\sqrt{2c}\,\sigma$ (dotted curve). For the evaluation of the constant a (mean effective radius of the ions), a curve was drawn through the experimental points and the origin, and from one value of j in the region of low concentrations (where the effect of the term cK is negligible) the values of σ and of the a corresponding were calculated. The constant a was found to have the value 4.41×10^{-8} cm. and K to have the value —0.0750. The points indicated by the circles containing crosses were obtained in a single series of experiments by Elliott, and were not consistent with the results of the other two series, the points for which are represented by

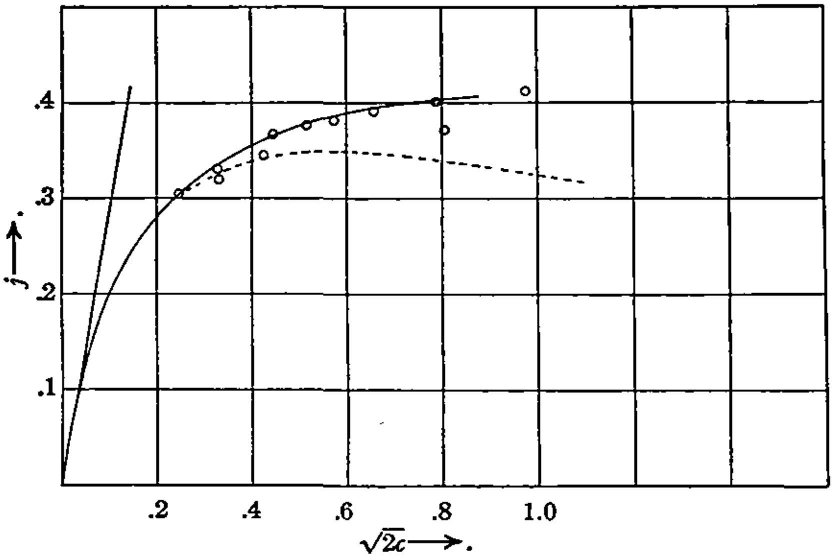

Fig. 5.—The relationship between j and the concentration of the solution for potassium iodide in liquid ammonia.

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[8] Elliott, *J. Phys. Chem.*, **28**, 611 (1924).

circles without crosses. The straight line intersecting the origin is the limiting tangent to the theoretical curve for the equation $j = 2.862\sqrt{2c}\,\sigma$.

The results for potassium iodide in liquid ammonia are shown graphically in Fig. 5. The solid curve represents the graph of the two-constant equation, with the constant $a = 5.76 \times 10^{-8}$ and $K = -0.1936$. In so far as these equations represent the values of j for sodium nitrate and potassium iodide in liquid ammonia, the mean activity coefficient of their ions may be calculated from the equation

$$\log_{10} f = \frac{-3.728\sqrt{2c}}{1 + 0.507 \times a\sqrt{2c} \times 10^8} + 2cK$$

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Summary

Freezing-point depressions of acetic acid containing dissolved lithium bromide, sodium bromide and sodium acetate have been measured and the results compared with the equation of Debye and Hückel. The experimental error in very dilute solutions is too great to permit the testing of the limiting law, but at greater concentrations the physical properties of the solvent and the effective radius of the ions are found to account satisfactorily for the results. The corresponding equation for the calculation of the activity coefficients is given.

The freezing-point depressions of acetic acid, containing electrolytes at concentrations sufficiently great that altered dielectric properties of the solvent are to be expected, have been compared with the equations of Debye and Hückel. An increase of the dielectric constant of the solvent is indicated. This result does not seem to be in agreement with the hypothesis of complete ionization, but is borne out by experimental measurements of the dielectric constants of non-aqueous solutions of electrolytes.

Freezing-point depressions of liquid ammonia containing dissolved electrolytes have also been compared with the theoretical equation. The theory is in agreement with the experiments in so far as the latter are consistent, but here also an increase of the dielectric constant of the solvent is indicated.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF UPSALA]

A NEW METHOD FOR DETERMINATION OF THE MOBILITY OF PROTEINS

BY THE SVEDBERG AND ARNE TISELIUS

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The mobility of egg albumin was determined by Svedberg and Scott[1] with the moving-boundary method, using the fluorescence of the albumin in ultraviolet light to make it visible. The mobilities determined were of about the size to be expected, and the iso-electric point was found to coincide with that found by other methods.

Some work upon the fluorescence of egg albumin performed in this Laboratory by O. Quensel[2] showed, however, that at least some of the fluorescence probably is not due to the albumin itself. The yellow-green fluorescence of the more acid solutions can be separated from the albumin. Possibly some substance partially adsorbed on the protein causes the fluorescence. It seemed, therefore, necessary to find another method of observing the moving boundary in order to test the results obtained by Svedberg and Scott.

All proteins have a very strong absorption in the ultraviolet of wave lengths lower than $300\mu\mu$. Light absorption, in general, is not so sensitive to minute changes in a system, and a considerable absorption is more likely to be caused by a considerable amount of a substance than is fluorescence. Photographing the moving boundary in ultraviolet light should, therefore, give a more reliable method. Moreover, Svedberg and J. B. Nichols in this Laboratory have made determinations of the molecular weight of egg albumin with the ultracentrifuge, using the ultraviolet absorption to determine the changes in concentration of protein produced by the centrifugal force. The value found by this method is in very good agreement with the value 34,000 generally accepted[3] and may therefore be regarded as proof of the applicability of the light absorption method, too.

In order to show the possibilities of the method we have made some measurements of the mobility of egg albumin in acetic acid–sodium acetate buffer solutions of different acidities. On account of the rather crude cataphoresis apparatus and camera used in the present investigation, the results are not of the degree of accuracy obtainable by this method and must be considered as quite preliminary. An apparatus allowing more accurate determinations is under construction.

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[1] THIS JOURNAL, **46**, 2700 (1924). See also Svedberg and Jette, *ibid.*, **45**, 954 (1923).

[2] Not yet published.

[3] See, for instance, Cohn, *Physiol. Rev.*, **5**, 3, p. 360 (1925). Sørensen, *Compt. rend. trav. Lab. Carlsberg*, **12**, 262 (1915–17).

The Apparatus.—As source of light a quartz mercury-vapor lamp of the vertical type (L, Fig. 1) furnished by Heraeus for use on 220 volts d. c. was used. It was mounted in a double-walled iron box, cooled by water circulating between the walls. The light first passed a water filter (W) to absorb heat radiated from the lamp, then a chlorine filter (C), that absorbs the part 300–380$\mu\mu$ of the ultraviolet,[4] then a mat screen (M) and the cataphoresis tube (T), a bromine filter (B) that absorbs the region 380–530$\mu\mu$ and the camera, (K).

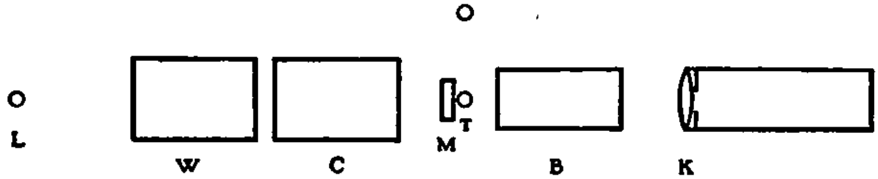

Fig. 1.—L, lamp; W, water cell; C, chlorine cell; M, mat screen; T, cataphoresis tube; B, bromine cell; K, camera.

The windows of the filters, the screen, the tube and the lens of the camera had to be made of quartz, because glass is opaque to the short-waved ultraviolet light used. The filters permit only light of wave lengths lower than 300$\mu\mu$ and higher than 530$\mu\mu$ to reach the camera. The sensitivity of an ordinary (not orthochromatic) photographic plate is however, much greater in the ultraviolet, and therefore the visible light that comes through does not interfere.

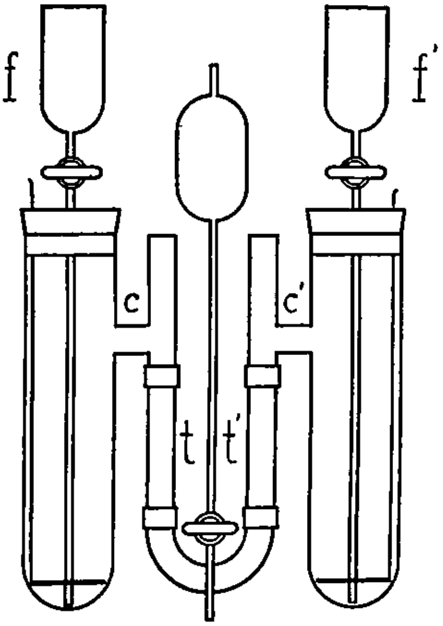

Fig. 2.—Cataphoresis apparatus; ff', funnels for the zinc sulfate solution; tt', quartz tubes.

The camera lens (K) had 205 mm. focal distance for the ultraviolet used. Just behind the lens was placed an 8mm. stop. The distance from cataphoresis tube to lens was the same as that from lens to plate, namely, 2 × 205 mm. Therefore, the tube and its image were of equal size. Afga Extra Rapid plates, $4^1/_2 \times 6$ cm., were used in the first experiments with 90 seconds' exposure. Later, Imperial Eclipse plates were used, making it possible to reduce the time of exposure to 15–20 seconds. In neither case could any blackening be obtained on the plate when a glass plate was used in front of the lens, allowing only the visible light to pass. With these short

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[4] Peskow, *J. Phys. Chem.*, **21**, 382 (1917).

times of exposure any decomposition of the albumin in the ultraviolet would seem improbable.[5]

The cataphoresis apparatus (Fig. 2) was of the ordinary U-tube type with reversible electrodes (zinc rods in a saturated solution of zinc sulfate). Some improvements over the apparatus used by Svedberg and Scott were made. First, the zinc sulfate solution was allowed to form a layer below the buffer solution before starting an experiment by causing it to flow slowly through the capillary tubes from the funnels ff′ until the electrodes were completely covered with sulfate. Second, the connections cc′ were made as short as possible. In this way the voltage necessary to produce a potential gradient of 1 volt per cm. in the U-tube could be reduced to 47.3 volts from 276.1 volts required in the Svedberg-Scott apparatus.

As mentioned above, it was necessary to use quartz for those parts of the apparatus where the boundaries migrate. Therefore it was made in parts, as shown in the figure: (1) the two electrode vessels with their side tubes; (2) the lower part of the U-tube with reservoir for the albumin, capillary and stopcock; (3) two specially selected quartz tubes tt′, as clear, uniform and free from bubbles as possible, that were connected with the other parts by rubber tubing; (1) and (2) were made of Jena "Normalglas." The whole apparatus was mounted on a wooden stand. Experiments were made in a room with sufficiently constant temperature.

The potential required was furnished by a storage battery of 50 volts. The voltage was measured with a precision voltmeter and was in general quite constant during the experiment. The current was only about 0.7 milliampere.

The resistance of the whole apparatus, when filled with 0.02 N potassium chloride solution and the same quantity of saturated zinc sulfate solution above the electrodes as was always used in the experiments, was $w = 33{,}210$ ohms at 16.0°. The cross section was determined by filling the quartz tube with water to different heights and weighing. The mean cross section in the part used was $q = 0.622$ sq. cm. From these data the potential necessary to produce a potential gradient of 1 volt per cm. in this part is $q \times w \times \kappa = 47.3$ volts, if κ be taken[6] as 0.002294 for 0.02 N potassium chloride at $t = 16.0°$. Since the resistance of the apparatus is inversely proportional to the conductivity of the solution in it, the product $w \times \kappa$ is always the same. Therefore, independent of conductivity, the potential 47.3 volts always produces unit potential gradient in the tube.

Materials.—The egg albumin used was prepared as in Svedberg and Scott's work, but the ordinary dialysis in collodion bags at 0° was interrupted after six days and continued in an electrodialyzer with parchment

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[5] Mond, *Pflüger's Arch.*, **196**, 540 (1922).

[6] Landolt-Börnstein-Scheele-Roth, "Tabellen," **1923**, p. 1098.

membranes and graphite electrodes according to Pauli.[7] After two days the conductivity was 1.6 × 10^{-5} mhos. The slightly yellow solution was filtered and kept in a Jena glass bottle in ice. The concentration of this stock solution was found to be 3.7% by drying a sample of 1 cc. at 105° to constant weight.

The curve in Fig. 3 shows the absorption coefficients at different wave lengths for a 0.1% solution of the egg albumin used. Variation of *P*H (4.0–4.8–5.6) had no perceptible effect on the absorption. The measurements were made with a Judd Lewis sector photometer.

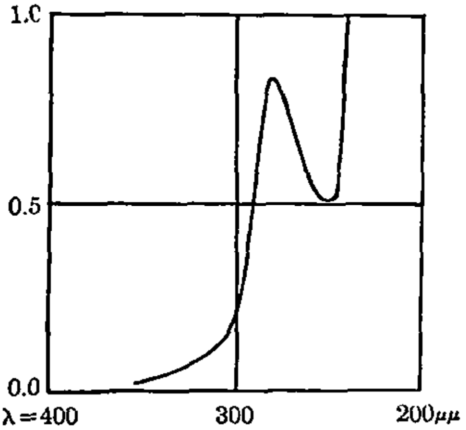

Fig. 3.—Absorption coefficient ($1/d$ × log I_0/I) at different wave lengths for a 0.1% solution of the egg albumin used.

The buffer mixtures were prepared from stock solutions of 0.2 *N* sodium acetate (Kahlbaum "Zur Analyse") and 1 *N* acetic acid. Toluene was added to the acetate as a preservative. The sodium acetate concentration was always 0.02 *N* both in buffer and buffer-albumin mixtures. The latter were always 1% with respect to albumin.

Sufficient acetic acid was added to give the same hydrogen-ion concentration in each. Under these conditions the conductivity on both sides of the boundary is also very nearly the same. This is a necessary condition for using the moving-boundary method in this form.

***P*H Measurements.**—The acidity was determined by the potentiometer method, the hydrogen electrode being measured against a 0.1 *N* calomel cell. The measurements were made at 16° and the Sørensen value (*P*H) calculated from the values *E* by the formula $P\text{H} = (E - 0.3382)/(0.0001984 \times 289)$ according to Sørensen.[8] The values of *E* obtained were always in close agreement with those calculated from tables. Measurements were made with solutions from *P*H = 3.40 to *P*H = 5.75.

A Typical Experiment.—When the solutions had been prepared and the Sørensen values measured, the apparatus was filled with buffer solution and the reservoirs were filled with the albumin-buffer mixture and zinc sulfate solution. The filled apparatus was allowed to stand overnight to attain uniform temperature. The experiment was started by opening the stopcocks for the sulfate; after about 20 minutes the stopcock for the albumin could be opened. In order to obtain a very slow rate of

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[7] Pauli, *Biochem. Z.*, **152**, 355 (1924).

[8] Sørensen, *Compt. rend. trav. Lab. Carlsberg*, **15**, 6 (1924).

flow in the beginning, which is very important for getting sharp boundaries, a very fine glass capillary was connected with the reservoir by a narrow rubber tubing. By using a set of capillaries of increasing diameter it is possible gradually to increase the rate of flow without disturbing the apparatus itself. When a sufficient volume had passed into the U-tube, the stopcock was closed. Now a photograph of the position of the boundary in the tube was taken, and the voltage was applied. It was impossible to photograph both boundaries with the arrangements used. Therefore, the boundary in most experiments, after having migrated a suitable distance in one direction was allowed to go back again by changing the direction of the current.

Fig. 4.—Migration of the boundary in an experiment.

All plates were developed over the same length of time. The measurements of movement were made on the plates, not on prints. Fig. 4 is a typical series of photographs for *P*H = 3.39, 48.9 volts, giving the position of the boundary after 0 minutes, 60 minutes, 120 minutes (change of direction of current), 55 minutes, 145 minutes. The corresponding distances as measured on the plates are 5.5, 11.0, 5.0, 11–12 mm. The last value is, however, very doubtful on account of the blurring of the boundary, and was not used. Generally the experiments were continued until the boundary became too diffuse. As values of v we get, after multiplying the measured distances by 0.983 (the ratio of the size of the tube to that of its image on the plate): $14.5 \cdot 10^{-5}$, $14.5 \cdot 10^{-5}$, $14.4 \cdot 10^{-5}$ ($12.6 \cdot 10^{-5}$) cm.^{2} sec.$^{-1}$ volt^{-1}. In general, the temperature was 13.5°; in only the last experiments was it somewhat higher (in the case mentioned 15.5°). To get comparable results all values were reduced to 13.5° by multiplying by $\eta_t/\eta_{13.5}$, η_t being the viscosity of water at t°.

TABLE I

*P*H	Mobility, $v \times 10^5$	Temp., °C.	$v \times 10^5$ at 13.5°
3.40	+14.5	15.5	+13.6
3.96	7.3	13.5	7.3
4.27	2.5	13.5	2.5
4.50	+ 1.3	13.5	+ 1.3
4.81	− 0.7	14.0	− 0.7
4.99	3.4	16.0	3.2
5.25	4.7	13.8	4.6
5.36	5.8	12.6	6.1
5.75	− 7.9	13.5	− 7.9

The values of *v* have been plotted against *P*H values in Fig. 5, Curve I. Evidently the iso-electric point occurs at 4.7. Curve II shows Svedberg and Scott's values, reduced to 13.5°. The very marked difference in form and position of the curves can probably not be explained by the small differences in experimental conditions only, but may be largely due to the properties of the fluorescence mentioned above. The errors of experiment seem to be less in the absorption experiments. In fact, it is much easier to get good pictures with very short times of exposure in the latter case. Fluorescence photography needs an exposure time of about 10 minutes, absorption photography only 15 seconds. Taking more than two pictures in the same fluorescence cataphoresis experiment, therefore, is very difficult, and the degree of accuracy accordingly lower.

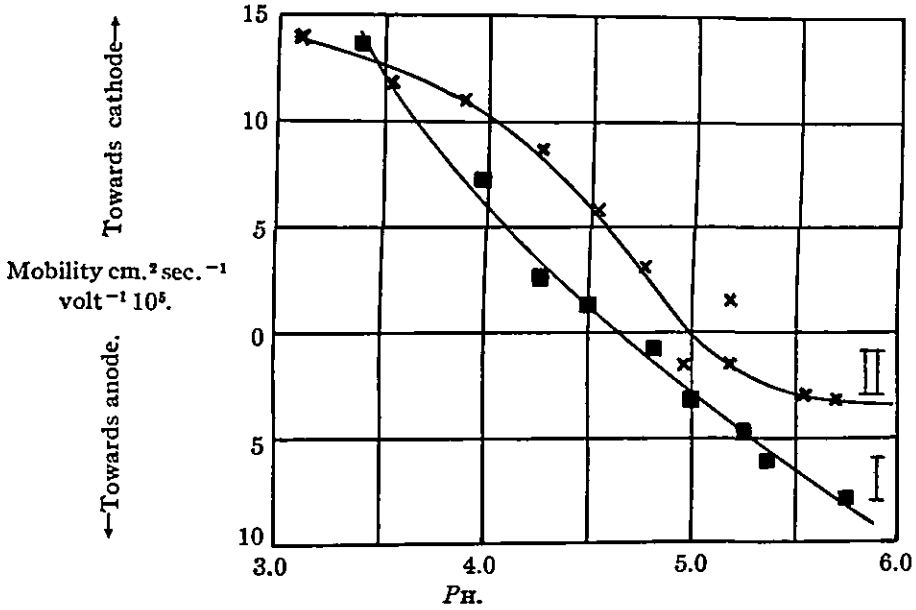

Fig. 5.—Values of the mobility obtained by the absorption (I) and by the fluorescence (II) method.

The expenses connected with these experiments have been defrayed by grants from the Foundation "Therese och Johan Anderssons Minne" and from the Nobel Fund of Chemistry.

Summary

It is proposed to study the mobility of proteins by the moving-boundary method, making the protein visible by photographing the cataphoresis tube in ultraviolet light of wave lengths below 300$\mu\mu$, obtained from a mercury lamp after passing through chlorine and bromine filters. The method is used in a preliminary study of the mobility of electrodialyzed egg albumin in a buffer mixture of acetic acid and sodium acetate of differ-

ent acidities. The mobility varied between 13.6×10^{-5} cm.^{2} sec.$^{-1}$ volt^{-1} towards the cathode at $P_H = 3.40$, and 7.9×10^{-5} cm.^{2} sec.$^{-1}$ volt^{-1} towards the anode at $P_H = 5.75$, all at $t = 13.5°$. The values obtained show some departure from those found by Svedberg and Scott using fluorescence to make the protein visible. It is shown that the absorption method is to be considered as more reliable.

Further work by this method with an improved apparatus is in progress.

Upsala, Sweden

[Contribution from the Chemical Laboratory of Harvard University]

OXIDATION POTENTIALS IN LIQUID AMMONIA INVOLVING QUATERNARY AMMONIUM RADICALS AND ALKALI METALS

By George Shannon Forbes and Curtis Elliott Norton

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This research was undertaken primarily to compare the oxidation potentials of systems of the type $NR_4 - \ominus \rightleftarrows NR_4^+$, where the R's are various alkyl groups. It appeared that such a potential series would be of value in the systematic study of alkyl groups and of quinquivalent nitrogen alike. Later we included the alkali metals, the better to correlate them with the quaternary radicals.

An examination of the literature indicated the difficulties of such an undertaking. Crotogino[1] electrolyzed water solutions of mono-, di- and trimethyl- and triethylammonium oxalates on a mercury cathode, and compared the positions of the breaks on the polarization curves. McCoy and Moore[2] prepared mono- and tetramethylammonium amalgams by electrolysis of solutions in absolute alcohol; the e.m.f. of their products measured against an aqueous calomel electrode varied with time. Podrouzek[3] electrolyzed water solutions of ammonium, tetramethyl and tetraethyl salts upon dropping mercury cathodes, obtaining results not very similar to those of Crotogino. Examination of the above-mentioned papers, and of papers on ammonium amalgams, revealed many objections to the use of mercury and to working temperatures above its freezing point. On the other hand, the literature concerning the preparation of quaternary ammonium radicals in liquid ammonia offered a better prospect of arranging the former in a potential series.

Palmaer[4] noted blue streaks near a cathode in a solution of tetramethylammonium chloride in liquid ammonia. Eleven years later Kraus[5] observed the same effect with tetramethyl and also with tetrapropyl salts.

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[1] Crotogino, *Z. Elektrochem.*, 7, 648 (1901).

[2] McCoy and Moore, This Journal, 33, 273 (1911).

[3] Podrouzek, *Rec. trav. chim.*, 44, 591 (1925).

[4] Palmaer, *Z. Elektrochem.*, 8, 729 (1902).

[5] Kraus, This Journal, 35, 1732 (1913).

Schlubach[6] and his associates have worked extensively upon quaternary ammonium radicals in liquid ammonia, electrolyzing chlorides or iodides at —70° in a vacuum. The products reduced iodine, sulfur, 2,6-dimethylpyrone, oxygen and acetylene. The blue radicals, on standing, yielded a colorless solution giving similar reactions. Substitution of hydrogen or of aryl groups increased instability, but Schlubach[6c] and Ballauf reported a colorless solution of free ammonium produced by the action of potassium on ammonium chloride in liquid ammonia. In addition, Schlubach and Miedel[6e] obtained tetra-ethylphosphonium, -arsonium and triethylsulfonium radicals.

Gibson and Argo[7] have investigated the spectra of alkali metals in liquid ammonia, and have shown that there is strong absorption in the red, as Schlubach and Ballauf also noted with quaternary ammonium radicals. The highly important work of Kraus and his associates upon alkali metals in liquid ammonia is discussed below.

Materials.—Tetramethyl- and tetra-ethylammonium bromides from the Eastman Kodak Company, and triethyl-*n*-butylammonium bromide kindly furnished by Professor C. S. Marvel of the University of Illinois were treated with silver oxide and the product was neutralized with hydriodic acid. In general, chlorides and bromides proved less satisfactory than iodides. Tetrapropylammonium iodide was purchased from Kahlbaum. We synthesized tetrabutyl-, methyltributyl-, trimethylbutyl-, tripropylbutyl- and ethyltributylammonium iodides from the proper tertiary amines and alkyl iodides. Diethyldibutylammonium iodide was prepared for us from dibutylamine and ethyl iodide by Mr. W. F. Hester of this Laboratory under the direction of Professor E. P. Kohler. We are very grateful for their kind coöperation. Two recrystallizations from water, or alcohol or acetone with centrifugal drainage yielded products cream-colored in most cases, which were dried over potassium hydroxide. Apparently diethyldibutyl, tripropylbutyl, methyltributyl and ethyltributyl salts have not hitherto been prepared. Like Hofmann and Reimer[8] we could not isolate a tetra-*iso*butyl compound. All products were analyzed by the Volhard method and had the proper iodine content within 0.5%.

Apparatus and Procedure.—Fig. 1 shows our cell in its final form. It made possible the preparation of solutions of quaternary iodides in liquid ammonia, electrolysis at —78° with rigorous exclusion of oxygen and moisture, measurement against a constant reference electrode of oxidation potentials of the systems $NR_4 - \ominus \rightleftarrows NR_4^+$, and determination of concentrations actually prevailing at the moment of such measurements.

The lower compartment E, shut off by the ground joint F, contained an electrode of silver foil M silver-plated and gently ignited, and was filled with liquid ammonia, distilled from sodium and saturated with silver nitrate carefully fused to eliminate moisture. Above the ground joint were two alundum cups I, surrounded by platinum gauze cathodes J. The cups contained the anodes K, connected in parallel, and some

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[6] Schlubach and others, (a) *Ber.*, 53, 1689 (1920); (b) 54, 1689, (c) 2811, (d) 2825 (1921), (e) 56, 1889, (f) 1892 (1923)

[7] Gibson and Argo, THIS JOURNAL, 40, 1327 (1918).

[8] Hofmann and Reimer, *Ber.*, 3, 757.(1870).

quaternary salt. Three pipets, N, contained carefully dried silver iodide rather than silver nitrate, as nitrates, we proved, oxidize the blue radicals. The platinum electrode L served for potential measurements only, but the gauze electrode showed the same e.m.f. a few seconds after cessation of electrolysis. If, however, the gauze electrode was connected alternately to dynamo and potentiometer by a rapidly revolving commutator, abnormally large and variable e.m.f. resulted. The stopper A of the cell was accurately ground; it bore the chimneys H and the inner tube C through which the various wires and tubes emerged.

Before being assembled, the cell was dried at 130° for several hours. Silver nitrate was dropped into E, and the joints were closed with sealing wax. The cell was heated for several hours more in a vertical tubular oven; meanwhile, there was passed through it nitrogen prepared by the Wanklyn process and purified with boiled sulfuric acid, properly aerated pentoxide and hot copper. After introduction of the quaternary iodide the cell was swept out for four hours more and then immersed in liquid ammonia in a Dewar vessel. By means of liquid nitrogen this bath could be maintained at the triple point of ammonia, —78°. Commercial liquid ammonia was treated with an excess of sodium in a glass-stoppered distilling flask, and the gas distilled through a trap into the cell. The lower compartment was entirely filled, also the upper one and the cups to the level I, but not the pipets. Electrolysis followed, using 40 to 25 volts and 0.05 to 0.2 ampere, varying with the solubilities of the several iodides. The e.m.f. of the cell $Ag^+ | AgNO_3 | NR_4\ NR_4I | Pt^-$ was measured with frequent agitation on an accurate Wolff potentiometer kindly lent by Professor Grinnell Jones. Readings of e.m.f. were referred to a standard Eppley cell. No interruption in the nitrogen current was

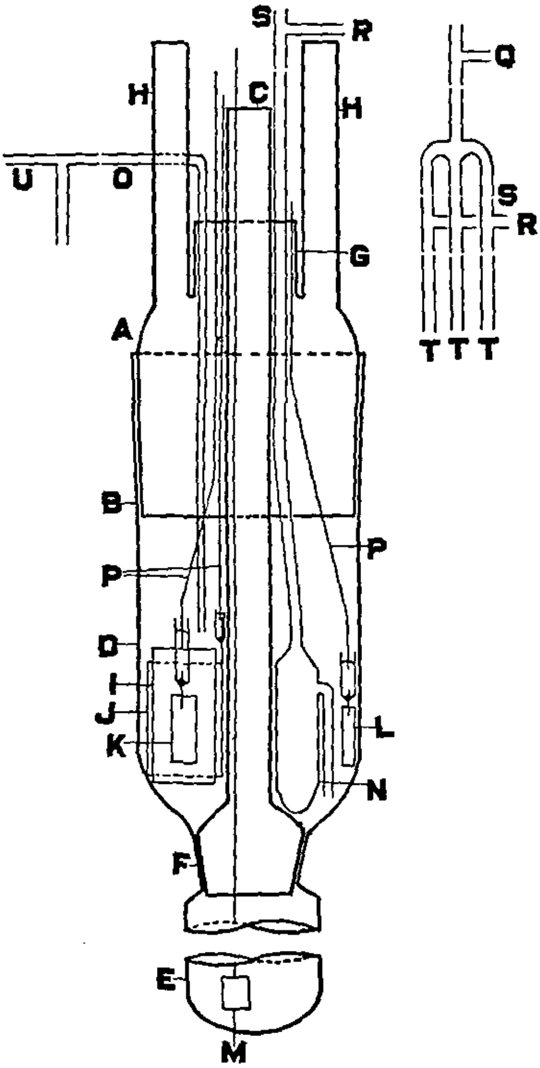

Fig. 1.—Cell for measurement of oxidation potentials.

tolerated. Much time was expended before our precautions were sufficient to prepare solutions giving readings constant within a few millivolts. These free radicals, we found, are vastly harder to handle than the alkali metals.

After the first measurement of e.m.f. one pipet containing silver iodide was filled with the blue solution by increasing the nitrogen pressure outside of it, and metallic silver was at once precipitated. Electrolysis, potential measurement and sampling were then twice repeated. Next, the cell was taken apart, and the position of the meniscus on each pipet was marked. After evaporation of the ammonia, the top of each pipet was cut off and the contents were transferred to a filter, the original volume of the sample being previously determined. After all soluble iodide had been washed out, the metallic silver was dissolved in dil. nitric acid and titrated according to Volhard, two end-points being secured in each case. As an excess of

TABLE I

CONCENTRATIONS AND ELECTROMOTIVE FORCES

Material	$[NH_4]$ ×10⁴	$[NR_4I]$ ×10⁴	E.m.f.	Material	$[NR_4]$ ×10⁴	$[NR_4I]$ ×10⁴	E.m.f.
$N(CH_3)_4I$	26	23	2.592	$N(CH_3)_3C_4H_9I$	32	1005	2.585
	26		2.594		41		2 594
	46		2.592		54		2.599
$N(C_2H_5)_4I$	29	105	2 594	$N(C_2H_5)_3C_4H_9I$	57	303	2 585
	36		2.597		55		2 596
	46		2.599		45		2 600
					63		2.597
					71		2.609
					51		2.612
$N(C_3H_7)_4I$	62	81	2.580	$N(C_3H_7)_3C_4H_9I$	12	46	2.580
	54		2 595		12		2 566
	41		2.590		23		2 581
	12		2.604		26		2.604
	42		2 612				
	32		2 603				
	09		2.605				
	16		2.613				
	27		2.613				
$N(C_4H_9)_4I$	16	39	2.558	$NCH_3(C_4H_9)_3I$	13	813	2.589
	24		2.579		14		2 596
	26		2.579		12		2.600
	38		2.592		13		2.594
	79		2 596		22		2.597
	24		2 593				
	45		2 599				
$N(C_2H_5)_2(C_4H_9)_2I$	*43*	*330*	*2.602*	$NC_2H_5(C_4H_9)_3I$	58	259	2.582
	12		2.607		40		2.591
	24		2.610		47		2.596
	16		2.607				
	15		2.608				
	32		2 614				

solid salt was always present after electrolysis, and as the cell was frequently agitated, its constant concentration was found by preparing new saturated solutions at —78° in Pyrex test-tubes, which were sampled as described above, and analyzed either by weighing the residue or by the Volhard method. The solubilities at —78° in moles per liter are given below in Table II with a probable error of 10%.

Table I gives actual measurements of e.m.f. and of concentrations in moles per liter in cells of the type $Ag^+ \mid AgNO_3$ satd. $\mid NR_4\ NR_4I \mid Pt^-$. $[NR_4]$ is here tabulated without allowance for dissociation into ion and electron, a point which is discussed below. All measurements in our final series are included.

Table II includes cells of the type $Pt \mid M + MINR_4 + NR_4I \mid Pt$ with the alkali metal M and its salt MI in Compartment E, also a third type of cell with two alkali metals.

TABLE II

QUARTERNARY RADICALS AND ALKALI METALS

$[N(C_2H_5)_2(C_4H_9)_2]$	$[N(C_2H_5)_2(C_4H_9)_2I]$	$[Na^+]$	$[NaI]$	Positive pole	E.m.f.
0.002	0.033	0.008	0.01	NR_4	0.006
.002	.033	1.0	.01	NR_4	.009
$[N(C_3H_7)_4]$	$[N(C_3H_7)_4I]$	$[K^+]$	$[KI]$	Positive pole	E.m.f.
0.003	0.0083	0.014	0.052	NR_4	0.005
.004	.0083	1.2	.052	NR_4	.018
.004	.0083	1.2	1.04	NR_4	.015
$[Li^+]$	$[LiI]$	$[Na^+]$	$[NaI]$	Positive pole	E.m.f.
0.02	0.002	0.08	0.002	Na	0.023
.10	.002	.08	.002	Na	.003
.10	.006	.08	.002	Na	.001

We now desired to reduce the above data to a consistent concentration basis. Because of limited concentration range of the radicals and errors in measuring e.m.f., the average value of $\Delta E/\Delta \log [NR_4]$ is a small negative quantity. Table II indicates that $\Delta E/\Delta \log [M]$ and $-\Delta E/\Delta \log [MI]$ are both very small. We also investigated $\Delta E/\Delta \log [NR_4I]$ by dropping into cells of the type first described additional quantities of quaternary iodides thoroughly dried and freed from absorbed air by pure nitrogen. The order of operations was electrolysis of an unsaturated solution sample, addition of salt to saturation, electrolysis, sample; addition of more salt, electrolysis, sample (see Table III).

TABLE III

CONCENTRATION EFFECTS

$[N(C_2H_5)_2(C_4H_9)_2]$	$[N(C_2H_5)_2(C_4H_9)_2I]$	E.m.f.	$[N(C_2H_5)(C_4H_9)_3]$	$[N(C_2H_5)(C_4H_9)_3I]$	E m.f.
0.0010	0.015	2.593	0.0022	0.020	2.604
.0010	.032	2.589	.0022	.059	2.595
.0005	.032	2 597	.0011	.059	2 605

The effect of doubling or trebling the concentration of an iodide is seen to be small. Even the sign of the correction is in doubt.

All the data, therefore, showed that the equation $E_0 = E + RT\,ln([NR_4]/[NR_4^+])$ was inadequate, at least, if concentrations were calculated from analytical data. Indeed, values of E_0 thus calculated for the several radicals stood in the same order as the solubilities of the corresponding quaternary iodides. Kraus's[9] theory of alkali metals in liquid ammonia, when extended to our radicals, suggested a more rational method of interpolation. Kraus holds that in such solutions (dilute) $Na + nNH_3 \rightleftarrows Na^+ + \ominus.nNH_3$, where the negative carrier is a solvated electron. He assumes that the electrons do no work at phase boundaries, and that potentials of *dilute* sodium concentration cells in liquid ammonia are determined solely by the junction potential, $E = (2nRT/F).ln[Na^+]_1/[Na^+]_2$. From his data we built up a curve from which the e.m.f. of any cell involving two sodium concentrations could be interpolated. Assuming analogous relations in concentration cells involving quaternary ammonium radicals, it appeared that the correction for $\Delta E/\Delta \log [NR_4]$, which we were unable to evaluate, should not exceed a few millivolts. The equilibrium $NR_4 - \ominus \rightleftarrows NR_4^+$ is peculiar in that any change in either concentration will tend to change the other in the same sense without transfer of electrons between solution and electrode. In consequence, the ratio $[NR_4]/[NR_4^+]$ is hard to vary through wide limits. As Kraus's sodium cells also were in a high degree reversible, the analogy thus renders void an argument against the reversibility of our cells, and also supplies one in its favor.

We have calculated very roughly the changes in junction potentials of our cells corresponding to a change in quaternary iodide concentration to 0.005 *M* in each case. We used the equation of Henderson, and assumed for lack of adequate data (1) that all mobilities are in the same ratio in water and in liquid ammonia at —35° or —78°; (2) that the "degree of dissociation" is invariably one-half; (3) that the total correction is half the sum of those calculated separately for variations in concentration of free radical and of quaternary iodide. The last column of Table IV embodies

TABLE IV

SOLUBILITIES AND CORRECTED E.M.F.

Radical	Soly. NR_4I at −78°	E.m.f. obs. av.	E m f. 0.005*M*	Radical	Soly. NR_4I at −78°	E m f. obs av.	E m f 0.005*M*
$N(CH_3)_4$	0.0023	2.593	2.585	$N(CH_3)_3C_4H_9$	0 10	2 592	2.590
$N(C_2H_5)_4$	.010	2.597	2.590	$N(C_2H_5)_3C_4H_9$	.031	2 600	2 595
$N(C_3H_7)_4$	.0083	2.602	2.596	$N(C_3H_7)_3C_4H_9$	.0063	2 583	2 578
$N(C_4H_9)_4$	.0039	2.585	2.578	$N(C_4H_9)_3CH_3$	.081	2.596	2 595
				Metal	MI		-
$N(C_2H_5)_2(C_4H_9)_2$	.033	2.597	2 595	Li	0 10	2.606	. .
				Na	.008	2 603	2.594
$N(C_2H_5)(C_4H_9)_3$	.059	2 601	2 599	K	05	2 601	...

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[9] Kraus, THIS JOURNAL, 30, 1323 (1908); 36, 864 (1914); 43, 749 (1921).

these very dubious corrections, also averaged oxidation potentials against the saturated silver-silver nitrate electrode, and averaged solubilities.

When all the alkyl groups are alike, solubility of the iodide reaches a maximum with the ethyl compound and then falls off again. The increased solubility of the mixed salts is striking, but the cases studied are not numerous enough to permit of a comprehensive generalization.

The oxidation potentials of quaternary radicals and of alkali metals alike in equilibrium with electrons and ions all lie within 25 millivolts. Ruff and Geisel,[10] investigating the possibility of compound formation between sodium or potassium and (liquid) ammonia, incidentally state "in the case of solutions of these metals, measurable electromotive forces do not appear." They do not, however, specify what cells were measured. The variation of our averaged values for the several radicals is considerably greater than the probable error in any given average. This implies that the composition of the radical or metal exerts a small but definite specific influence upon its oxidation potential. We have thus far been unable to correlate this influence with composition, except to note that lithium, as Lewis and Keyes[11] found, appears to be the most electropositive. We prefer, therefore, to emphasize the approximate identity of oxidation potentials of quaternary radicals and of alkali metals, in the presence of their iodides, and the similarity between the fifth valence of nitrogen and that of the alkali metals, which is more strikingly demonstrated here than in any previous electrochemical research.

In addition to acknowledgments made above, we express our appreciation of a grant from the Milton Fund for Research, of liquid nitrogen furnished gratis by the Air Reduction and Sales Company, and of information about quaternary ammonium halides supplied by Professors E. P. Kohler and J. B. Conant.

Summary

An apparatus and a method have been devised for measurement of oxidation potentials of ten quaternary ammonium radicals in equilibrium with their ions and electrons on platinum against silver electrodes in saturated silver nitrate solution, all in liquid ammonia at its triple point. Comparisons with alkali metals were also made.

The concentrations of free radicals were determined in terms of silver, after reaction with silver iodide. The concentrations of the corresponding halides in saturated solution at —78° were also determined. The analytical errors were of the order of 10%.

The observed oxidation potentials of the radicals, also of lithium, sodium and potassium, all lie within 25 millivolts of one another. This

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[10] Ruff and Geisel, *Ber.*, 39, 828 (1906).

[11] Lewis and Keyes, This Journal, 35, 340 (1913).

outcome upholds the analogy between the fifth valence of nitrogen and that of an alkali metal.

Data necessary to reduce all results to a comparable concentration basis are not available, but evidence is given that the corrections should be reckoned in millivolts rather than in centivolts.

The small differences in oxidation potentials, if conditioned by chemical composition, are not readily correlated with the latter.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

THE FREE ENERGY AND HEAT OF TRANSFER OF BARIUM IN ITS LIQUID AMALGAMS

BY PAUL A. ANDERSON

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The electromotive measurement of a series of liquid-amalgam concentration cells is capable of furnishing quite exact information regarding both the thermodynamic properties of the system and the specific state of the metal solute in its mercury solution. While this type of investigation has been extended to many of the commoner mercury-soluble metals, none of the amalgams of the alkaline earth group of metals has been subjected to satisfactorily exact study. Such a study of barium amalgam was the object of the work to be described.

The two general methods available for determination of the electromotive forces of concentration cells of the reactive alkali and alkaline earth amalgams involve, respectively, measurement in an aqueous electrolyte with the use of some form of renewable electrode, and measurement in some non-aqueous electrolyte that does not decompose the amalgam. Richards and Conant[1] applied the former method to sodium amalgam concentration cells and by the use of synchronously flowing drop electrodes obtained reproducible potentials down to a concentration of 0.17 atomic per cent. of sodium. Cady[2] applied the second method in his measurements of two cells of the type: Ba amalgam (C_1), BaI_2 in pyridine, Ba amalgam (C_2). Comparison of Cady's analyses with the solubility data of Kerp and Böttger[3] indicates that the amalgam of his concentrated electrode was highly supersaturated. His results, therefore, are of only qualitative significance.

Examination of Electrolytes

The problem involved in the measurement of the potentials of barium amalgam concentration cells was found to resolve itself largely into a

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[1] Richards and Conant, THIS JOURNAL, 44, 601 (1922).

[2] Cady, *J. Phys. Chem.*, 2, 551 (1898).

[3] Kerp and Böttger, *Z. anorg. Chem.*, 25, 1 (1900).

search for a satisfactory electrolyte. The criteria for such an electrolyte are (1) an electrical conductance sufficiently high to allow accurate potentiometric measurement of the cell, and (2) a rate of reaction with the amalgam sufficiently low to bring the measurements within the limits of constancy and reproducibility required for their adequate interpretation. The facts that liquid barium amalgam saturated at 25° contains only 0.27 atomic per cent. of barium and that most of the measurements must be made upon very dilute amalgams emphasize the importance of the second criterion for the case in point.

Six electrolytes have been examined in the course of this work: (1) aqueous barium hydroxide prepared from barium amalgam and conductivity water, (2) ethyl alcohol-barium iodide, (3) *n*-propyl alcohol-barium iodide, (4) pyridine-barium iodide, (5) ethylamine-barium iodide, and (6) hydrazine-barium chloride. The preparation of the materials employed in the cell finally adopted for study is described below in detail; all other materials were purified by conventional methods. Each of the non-aqueous solvents was intensively dehydrated after purification and allowed to stand over barium amalgam for a month to a year before it was introduced into a cell. Electrolytes 1, 2 and 3 were tested in a modified form of the Richards and Conant[1] apparatus with closed electrode compartment and found to react with the barium at a rate that precluded a more than approximate estimate of potentials. With the pyridine electrolyte in this cell the potentials were found to fall rapidly, a behavior unique among the electrolytes studied and similar to that observed by Richards and Garrod-Thomas[4] for a pyridine-lithium chloride solution. The ethylamine-barium iodide electrolyte was tested in a cell comprising three non-renewable electrodes each composed of about 40 cc. of amalgam. Shortly after introduction into the cell this solution precipitated its barium iodide with consequent lowering of its conductance to a value too low to permit a reliable estimate of potentials.[5]

In the further search for a satisfactory solvent, anhydrous hydrazine suggested itself on the basis of its high dielectric constant and probable inertness toward barium amalgam. An intensively dehydrated solution of barium chloride in this solvent has permitted the attainment of a constancy of ± 0.001 mv. (millivolt) in the measurement of barium amalgam concentration cells.

Experimental Methods

Materials.—Mercury was purified by repeated spraying through a 2-meter tower, two distillations in a current of air, and one in a vacuum. Barium chloride was precipitated twice by gaseous hydrogen chloride and once by redistilled ethyl alcohol with thorough centrifuging of each precipitate. The hydrogen employed in washing out and

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[4] Richards and Garrod-Thomas, *Carnegie Inst. Pub.*, No. 118 (1909).

[5] Lewis and Keyes, THIS JOURNAL, 34, 119 (1912).

filling the cell and reservoirs was obtained from a Richards zinc amalgam generator and purified by passage through solid potassium hydroxide, neutral permanganate solution, hot platinized asbestos, and phosphorus pentoxide in an all-glass system.

Five hundred g. of a 33% aqueous solution of hydrazine monohydrate was partially dehydrated by the method of Raschig.[6] Dehydration was completed by refluxing over crude barium oxide for eight hours in an atmosphere of hydrogen by the method of Lobry de Bruyn[7] and of Hale and Shetterly.[8] The final distillate of anhydrous hydrazine was collected in a receiver over a quantity of barium amalgam and sufficient anhydrous barium chloride, estimated from the data of Welsh and Broderson,[9] to give a nearly saturated solution at 15°, the lowest temperature at which measurements were made. The receiver was ground to fit both the condenser and a delivery tube. The latter, which was fitted with a glass-wool filter and mercury-sealed, ungreased stopcock, was introduced against a stream of dry hydrogen after completion of the distillation. The receiver thus served as the electrolyte reservoir without necessity of further transfer. The solution was allowed to stand over the barium amalgam for a month before introduction into the cell.

Preparation and Analysis of Amalgams.—The amalgams were prepared by electrolysis of a saturated solution of barium chloride between a mercury cathode and platinum anode, carried out in a separatory funnel from which the amalgam could be conveniently withdrawn. The amalgam was shaken with three changes of conductivity water, partially dried by filter paper, drawn into an evacuated reservoir and stored under hydrogen. Traces of water and oxygen were removed by reaction with the amalgam itself and the small amount of barium oxide thus formed removed incidentally to the introduction of the amalgam into the cell.

Triplicate analyses were made after each set of potential measurements. Samples, varying in amount from 50 to 150 g. with the dilution of the amalgam, were run from the cell directly into a slight excess of standard hydrochloric acid and the excess was titrated back with standard barium hydroxide solution after decomposition was complete. The mercury was dried in a vacuum desiccator and weighed. Bromothymol blue was used as indicator and weight burets were employed exclusively in titration. Analyses were reproducible to within 0.1% in the case of the more concentrated and within 0.5% for the more dilute amalgams. The probable accuracy of the analyses is of the same order, with the single exception of the most dilute amalgam measured, observed mole fraction 0.000158, which is given special consideration below.

The Cell.—The cell employed (Fig. 1) consists essentially of three amalgam reservoirs, R, R′ and R″, communicating by 1-mm. capillary tubes with renewable electrodes E, E′ and E″, which were sealed into the closed electrolyte chamber V. One of the reservoirs was equipped with a magnetic stirrer S consisting of a soft iron armature completely enclosed

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[6] Raschig, *Ber.*, **43**, 1927 (1910).

[7] Lobry de Bruyn, *Rec. trav. chim.*, **14**, 83, 88 (1895); **15**, 174 (1896).

[8] Hale and Shetterly, This Journal, **33**, 1071 (1911).

[9] Welsh and Broderson, *ibid.*, **37**, 816 (1915).

by Pyrex glass blown in the form shown. The dimensions of this stirrer were such that it floated in the position depicted when at rest. F, F′ and F″ are capillary filter tubes of 0.2mm. bore through which the amalgams were introduced into the cell. The upper ends of these tubes were ground to fit the amalgam storage reservoir. The tube P fitted with platinum glower and containing a small quantity of phosphorus pentoxide served to remove any trace of oxygen present in the incoming hydrogen. The pressure of hydrogen within the cell was regulated by a mercury leveling bulb connected at T to the mercury chamber Q. The electrolyte chamber V was sealed to the electrodes at an inclination of about 20° to the horizontal; the amalgam overflowing from the electrodes thus collected in the small well at the lower end of the chamber and could easily be drawn off as it accumulated. The electrode orifices were blown in the form of small cups, a design found preferable to that of Richards and Conant when a continuous synchronous flow of amalgam is not required. The 3-way stopcocks placed between the reservoirs and electrodes served to regulate the supply of amalgams to the latter and to furnish a convenient means of drawing off analysis samples at D.

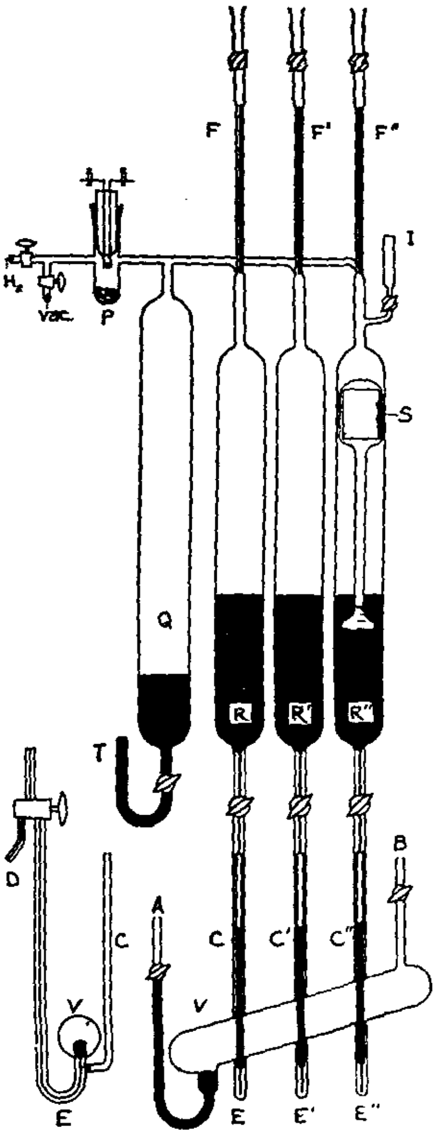

Fig. 1.

Procedure.—The cell was examined for pinhole leaks by the spark test, thoroughly cleaned and dried, and the stopcocks were lightly greased. After repeated alternate evacuation and filling with pure, dry hydrogen, Reservoirs R and R″ were filled with amalgam of concentration slightly less than that corresponding to saturation at 15°. R′ was filled with a relatively dilute amalgam. The complete exclusion of air and moisture during the filling operation was proved by the fact that the amalgam surfaces retained the appearance of pure mercury for some time after the measurements were completed. The amalgams in R and R′, to be designated hereafter as Amalgams A and B, respectively, remained at constant concentration throughout the run. The amalgam in R″, Amalgam C, was progressively diluted by small increments of mercury introduced at I. Mixing of the diluted amalgams was effected by the application of a portable bipolar electromagnet, by which the iron-cored stirrer was forced to move rapidly down and up. The efficacy of this mixing method was attested by the fact that the triplicate analyses of Amalgam C, made upon samples drawn successively from the reservoir, invariably checked within the limit of reproducibility for an unquestionably homogeneous amalgam of the same concentration. The magnetic-stirring method thus provided for the preparation, *in situ*, of an indefinitely extensive series of amalgams of progressively increasing dilution. Any advantage that this method may have is contingent upon the delivery at the electrode orifice of amalgam truly representative of the bulk of Amalgam C in the reservoir. This point was easily tested by following the potential between E″ and one of the electrodes of constant composition. It was found that the withdrawal of 10 cc. of amalgam from the orifice of Electrode E″ invariably brought the concentration at the orifice to that of the bulk of amalgam in the reservoir, further withdrawal of amalgam producing no detectable change of potential. The error introduced by the use of this method is perhaps less than that involved in the graphical combination of a series of measurements upon individual amalgam pairs while the manipulative advantage is decided. At each dilution of Amalgam C the potentials of two concentration cells were obtained. The use of two reference electrodes not only furnished a check upon the consistency of each set of readings but also, by preventing any possible variations in composition, and hence potential, of either of the reference amalgams from passing unnoticed, furnished a valuable check upon the reliability of the whole series of potential values recorded during a run.

Electromotive-Force Measurements

Measurements of the potentials of 23 concentration cells have been made at 25.00° ± 0.05° over the concentration range 0.2629, slightly below saturation, to 0.0108 weight per cent. of barium. Three cells of composition chosen to cover most of this concentration range have also been measured at 15° and 35°. By direct subtraction of observed potentials, made possible by the use of the reference electrodes, data for 55 more cells are made available without recourse to graphical interpolation.

The conductance of the hydrazine-barium chloride electrolyte was sufficiently high to permit potentiometric measurement to 0.001 mv. (millivolt) and its rate of reaction with the amalgam very low. In the case of the more concentrated amalgams, the initial potentials between freshly renewed electrodes remained constant within 0.001 mv. during the time required for a series of readings and within 0.01 mv. for several hours, while even in the most dilute amalgam measured, which contained one part of barium in ten thousand of amalgam, the variation did not exceed a few microvolts during the reading time. The readings were reproducible within 0.005 mv. after renewal of all the electrodes and the consistency as shown by cross checks between the three electrodes fell within this limit.

The electromotive-force measurements at 25.00° ± 0.05° are recorded in Table I to the nearest 0.005 mv. In the cell designation, the positive electrode is given first and the dilutions of Amalgam C are indicated by Roman numerals. As stated above, C I was of the same concentration as Amalgam A.

TABLE I

SUMMARY OF OBSERVED ELECTROMOTIVE FORCES AT 25°

Electrodes		Amalg C, Wt. % of Ba	E.m.f., mv.	Electrodes		Amalg C, Wt. % of Ba	E m.f., mv.
C II	A	0.2362	2.050	B	CII	0.2362	10.855
C III	A	.2085	4.270	B	CIII	.2085	8.645
C IV	A	.1783	7.005	B	CIV	.1783	5 910
C V	A	.1496	9.850	B	CV	.1496	3.055
B	A	....	12.910	C VI	B	.1160	1.050
C VI	A	.1160	13.965	C VII	B	.08994	4.950
C VII	A	.08994	17.865	C VIII	B	.06804	9.080
C VIII	A	.06804	22.000	C IX	B	.05033	13.335
C IX	A	.05033	26.240	C X	B	.03106	19.980
C X	A	.03106	32.890	C XI	B	.01894	26.625
C XI	A	.01894	39.530	C XII	B	.01083	34.210
C XII	A	.01083	47.125				

Reference Amalgam A: 0 2629% of Ba by wt.
Reference Amalgam B: 0.1228% of Ba by wt.

The electromotive force-concentration curve of the A-C series of cells with the potential of Reference Amalgam A taken as zero is given in Fig. 2. When the potential for the cell composed of Reference Amalgams A and B, indicated by the crossed circle, was plotted upon this graph it was found to fall upon the curve representing the change of potential of A toward C with the dilution of the latter, a fact which affords quite conclusive evidence for the reliability of the dilution method employed.

Free Energy of Transfer and Activity of Barium

The third and fourth columns of Table II present the comparison of the observed potentials for the A-C series of barium amalgam cells with the potentials calculated by the simple concentration law $E = [RT/nF \cdot ln(N_2/N_2')]$. It is apparent that the law fails to account for the observed electromotive forces, which are markedly higher than the calculated values. As would be expected, the deviations increase with the dilution ratio and, for a given dilution ratio, decrease with the concentration. The positive sign of the deviations is in accord with Ramsay's observation[10] that

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[10] Ramsay, *J. Chem. Soc.*, 55, 521 (1889).

barium lowers the vapor pressure of mercury to a much greater degree than Raoult's law requires. Further, for the range of atomic concentrations involved, barium amalgam exhibits a greater deviation from the concentration law than any of the numerous amalgams previously investigated.

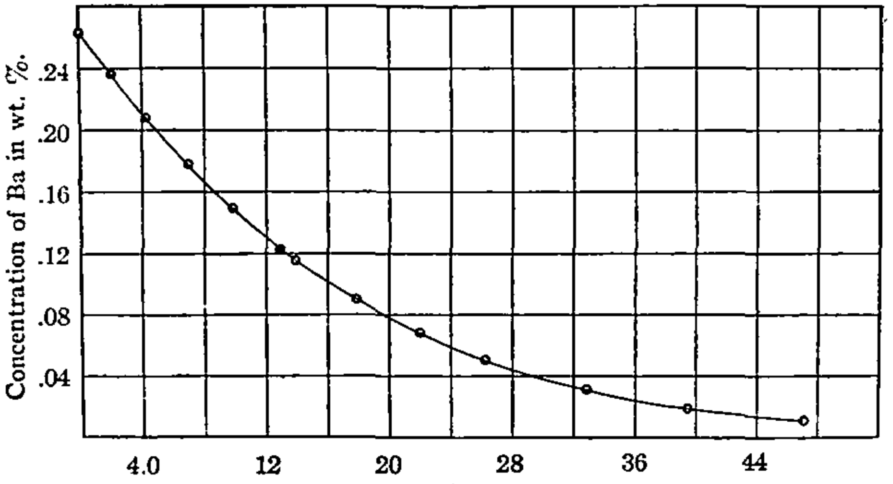

Fig. 2.

TABLE II

FREE ENERGY OF TRANSFER AND ACTIVITY OF BARIUM

Electrode	Mole fraction of Ba (N_2) $\times 10^3$	E.m.f., Obs.	Mv., Calcd.	Activity of barium (a_2)	a_2/N_2	$-\Delta F$, Calcd.
A	3.835	0 00	0.00	0.006209	1.619	00
C II	3 448	2.05	1.37	.005293	1.535	95
C III	3 041	4.27	2.98	.004453	1.464	197
C IV	2.604	7.01	4.98	.003599	1.383	323
C V	2.183	9.85	7.24	.002884	1.321	455
C VI	1.693	13.97	10.50	.002093	1.236	644
C VII	1 312	17.87	13.78	.001547	1.179	824
C VIII	0.993	22 00	17.35	.001121	1.129	1015
C IX	.734	26 24	21.23	.000805	1.097	1211
C X	.453	32.89	27.43	.000480	1.060	1518
C XI	.276	39.53	33.78	.000286	1.035	1824
C XII	155*	47.12	41.18	.000158	1.019	2174
			∞	.0	1.0	

The thermodynamic treatment of solutions that do not conform to Raoult's law at solute concentrations practicable for experimental investigation has been facilitated by the use of the so-called activity function. The electromotive force of an amalgam concentration cell is given, according to the definition of this function, by the equation $E = -(RT/nF)ln(a_2/a_2')$, where a_2 and a_2' for the case in point are the activities of barium in the concentrated and dilute electrodes, respectively. The extrapolation of the data of the second and third columns of Table II is carried out by the method of Lewis and Randall[11] in Fig. 3. It is interesting to note that the curve approximates closely to a straight line and that log (a_2/N_2), therefore, is apparently a straight-line function of N_2. Eleven of the twelve points fall close to the curve. The point for Amalgam C XII is probably low and, since no tendency to downward flexure is apparent in preceding points, has been disregarded in the extrapolation. The deviation of this point probably is to be attributed to an error in analysis corresponding to an error of 3×10^{-6} in the mole fraction of barium. The probable correct value of 0.000155 indicated by the curve has been substituted for the observed value of 0.000158 in Table II and indicated by an asterisk.

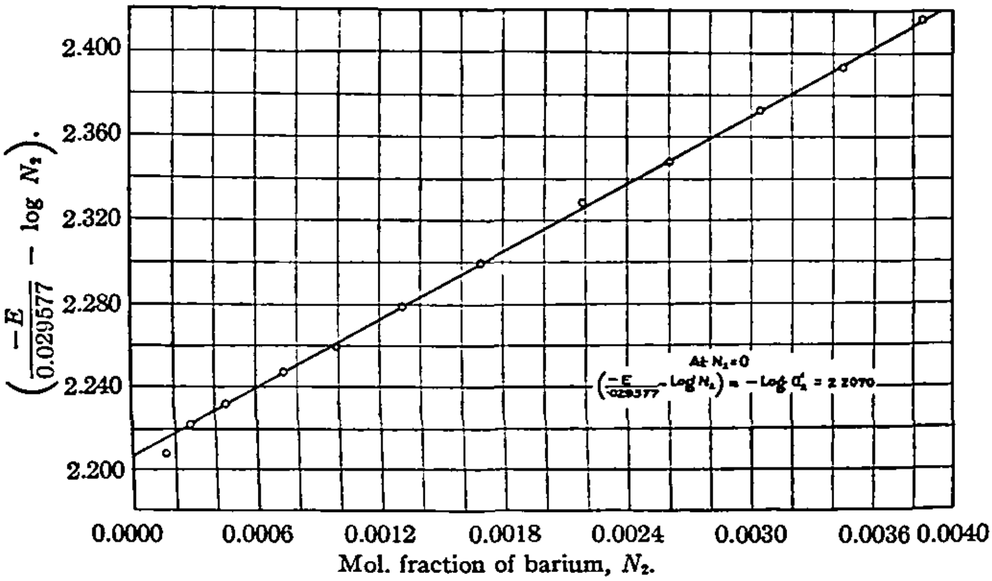

Fig. 3.—Extrapolation of data for activity of reference amalgam.

The activity values are tabulated in Col. 5 and the activity-mole fraction ratios in Col. 6 of Table II. In the last column are tabulated the computed values for the free-energy decrease attending the transfer of one mole of barium from an infinitely large quantity of Amalgam A to an infinitely large quantity of each of the more dilute amalgams.

The Heat of Transfer of Barium

The results of a careful measurement of three cells at 15°, 25° and 35° are recorded in Table III.

$\Delta E/\Delta T$ is in each case slightly higher between 25° and 35° than between 15° and 25°. In the case of the more dilute C X-B cell this difference is of the order of reproducibility of potentials, but in the other cells is quite unmistakable. The temperature coefficient of electromotive force for

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[11] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, p. 265.

TABLE III

TEMPERATURE COEFFICIENTS OF ELECTROMOTIVE FORCE

Electrodes	E.m.f., mv. 15°	 25°	 35°	$\Delta E/\Delta T$, mv. 15–25°	 25–35°	 15–35°
C X-B	19.355	19.980	20.610	0.0625	0.0630	0.06275
C X-A	31.935	32 890	33.890	.0955	.1000	.09775
B-A	12.590	12.910	13.290	.0320	.0380	.03500

barium amalgam concentration cells is, therefore, apparently a function of the temperature; d^2E/dT^2 is positive and, as would be expected, increases with the concentration. The heats of transfer computed by the Helmholtz equation $-\Delta H = nFE - nF(dE/dT)T$ are recorded in Table IV. Since the change of volume attending the transfer process probably is small, $-\Delta H$ represents quite accurately the total energy decrease undergone by the system. That the heat of transfer is not, in general, equal to the heat change involved in the dilution of Amalgam C_1 by pure mercury, a quantity determinable only by thermochemical measurement, has been pointed out by Richards and Daniels.[12]

TABLE IV

THE HEAT OF TRANSFER OF BARIUM

Ba, % by wt. C_1	 C_2	$E^{25°}$, mv.	$\frac{dE}{dT}$ 15–35°, mv./degree	nEF, joules	$nFT(dE/dT)$, joules	$-\Delta H$, joules
0.1228	0.03106	19.980	0.06275	3856	3610	246
.2629	.1228	12.910	.03500	2492	2014	478
.2629	.03106	32.890	.09775	6347	5623	724

The heat of transfer of barium is of the same sign as that of sodium[1] and of thallium and indium[13] and is of opposite sign to that of zinc, tin and lead.[4] For the range of atomic concentrations involved, its magnitude is greater than that of any of the amalgams previously investigated, a result consistent with the greater deviations of barium amalgams from the concentration law.

Recognizing the failure of the unmodified concentration formula to account for the electromotive forces of the amalgam concentration cells that he had under observation, Cady[2] proposed to equate the electrical energy not to the osmotic energy alone but to the sum of the osmotic energy and the heat of dilution of the solute metal, or $nFE = RT\ ln$-

TABLE V

APPLICATION OF DATA TO TEST CADY EQUATION

Ba, mole fraction N_2	 N_2'	E.m.f., mv. at 25° Obs.	 Concn. law	 Cady eq	Deviations Concn. law	 Cady eq.
0.003835	0.001792	12.91	9.77	12.25	3.14	0.66
.001792	.000453	19.98	17.65	18.92	2.33	1.06
003835	.000453	32 89	27.42	31.18	5.47	1.71

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[12] Richards and Daniels, THIS JOURNAL, **41,** 1761 (1919).

[13] Richards and Wilson, *Carnegie Inst. Pub.*, No. **118** (1909), p. 34.

$(N_2/N') + U$. U is to be identified with the corresponding term, $-\Delta H$, of the Helmholtz equation and like the latter represents the heat of transfer rather than, as assumed by Cady, the heat of dilution of the solute. Table V records the results of the application of Cady's equation to the data of the present investigation.

While the Cady equation is evidently more successful than the simple concentration formula, the deviations from it are much greater than the probable experimental error and are more marked than in any amalgam system yet investigated at equivalent atomic concentration. Departures from the Cady equation are to be attributed to one or both of at least two factors; (1) a failure of the stoichiometric osmotic energy term to represent the actual osmotic effect; (2) a heat-capacity change attending the transfer of solute.[14] In the present case the first factor, presumably due to the formation of hydrargyrates of type formula Ba_mHg_n is responsible for nearly all of the deviation. A simple relation, apparently overlooked heretofore, that exists between the change of heat capacity and d^2E/dT^2 may be utilized to determine from electromotive data alone the sign and order of magnitude of the second factor. Combination of the differentiated Helmholtz equation, $d\Delta H/dT = nFT(d^2E/dT^2)$, with the Kirchhoff equation gives $\Delta C_p = nFT(d^2E/dT^2)$. A positive value of d^2E/dT^2 indicates an increase in heat capacity and *vice versa.* The lack of equality between the temperature coefficients of amalgam concentration cells for low and high ranges, which has frequently been observed and often assigned to experimental error only is, then, presumably to be expected on theoretical grounds. The present measurements indicate that d^2E/dT^2 is positive for barium amalgams, that the free-energy change associated with the chemical effect in the transfer of barium is slightly greater than the change in heat content, and that, in consequence, the part of the observed potential due to the chemical reaction is greater than the value given by the heat of transfer term of the Cady equation. Both of the factors that condition the deviation from the Cady equation, then, apparently operate to make the observed potential greater than the calculated value.

I wish to express my indebtedness to Professor Theodore W. Richards under whose direction the major part of this work was carried out.

Summary

1. The experimental conditions required for an exact electromotive study of liquid barium amalgam concentration cells have been worked out. By the use of a solution of barium chloride in anhydrous hydrazine as electrolyte a constancy and reproducibility of well within 0.01 mv. has been obtained in the measurement of potentials.

2. Twenty-three cells have been measured at 25° over the concentra-

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[14] Richards, *Proc. Am. Acad. Arts Sci.*, **38**, 308 (1902).

tion range 0.2629, slightly below saturation, to 0.0108 of barium by weight. Three cells have also been measured at 15° and 35°.

3. The observed potentials are markedly higher than the values calculated by the concentration law. The data are extrapolated to infinite dilution and the activities of barium calculated. The free energies of transfer are computed.
4. The heats of transfer of barium are calculated. The temperature coefficient of electromotive force is apparently a function of the temperature and d^2E/dT^2 positive.
5. The data are applied to test the Cady equation.

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[Contribution from the Research Laboratory of Organic Chemistry, Massachusetts Institute of Technology No. 8]

THE COLOR OF THE TERVALENT TITANIUM ION

By Jean Piccard

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In inorganic chemistry as well as in organic chemistry there are methods which enable us in certain cases to deduce the color of a compound from its formula. Piccard and Thomas were able to predict that certain salts which are usually considered as colorless should be yellow when observed in sufficiently thick layers. This proved to be the case with cadmium iodide and with mercury dibromide.[1]

In the present paper we shall see the reverse case, that of an ion which is perfectly colorless although generally considered as being violet.

In the textbooks of inorganic chemistry we are told that—with the exception of certain complex salts which are yellow or green—tervalent titanium gives violet solutions. Incidentally, I have made the observation that the violet solution of titanium trichloride becomes much more strongly colored when one adds ammonium thiocyanate to it. Titanium thiocyanate is an intensely violet molecule or complex and the suspicion arose that perhaps titanium trichloride solutions may also owe their color not to the titanium ion but to the titanium trichloride molecule. We can easily confirm this hypothesis if we take two *flat-bottom test-tubes with 2 cc. of a* 0.025 *N* titanium trichloride solution in each. We place these tubes side by side while we look vertically down through them. Then if we add water to one of the test-tubes we immediately notice that the color in the dilute solution diminishes, and after an addition of 20 cc. of water the violet color has disappeared.[2] The law of Beer is not followed,[3] and it is proved

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[1] Piccard and Thomas, *Helvetica Chim. Acta*, 6, 1040 (1923).

[2] This phenomenon is not due to hydrolysis, because it can also be observed when we dilute with weak hydrochloric acid solution, so that the hydrogen-ion concentration remains constant or even increases. Also, hydrolysis would increase the color,

beyond any doubt that the tervalent titanium ion is colorless or nearly colorless (we have not yet observed very deep layers) and that the well-known violet color of titanium trichloride solutions is a molecular property of titanium trichloride or of a complex like $[TiCl_5]$. The addition of concd. hydrochloric acid represses the dissociation and the violet color reappears.

This experiment shows that the Ti^{III} ion, like the chloride ion, has a *latent color* according to the definition given by Piccard and Thomas.[4] Since the fluoride ion has no latent color at all, the addition of hydrofluoric acid to a solution of titanium trichloride should take its violet color away and indeed it does.

In our first publication we did not attempt to give any theoretical explanation for the described observations. We said: "Notre petite étude est purement empirique." Professor Fajans was kind enough to draw our attention to two of his publications[5,6] in which he gives a theoretical explanation of the fact that the color of a salt may change if one replaces in it a colorless ion by another colorless ion. To use his expressions we can formulate our observation with the following words.

The tervalent titanium ion is colorless, but titanium trichloride is colored, because the titanium atom deforms the electronic shells of the chloride ions.[7]

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not decrease it, because OH has a much stronger latent color than Cl, and $Ti(OH)_3$ *is nearly black. That the phenomenon is not due to oxidation or liberation of free* hydrogen was shown by titration with permanganate. In both test-tubes exactly the same amount of $KMnO_4$ is needed to produce a pink coloration.

[3] When one makes the same experiment with a copper sulfate solution, one does not see any change of color, because it is the (hydrated) Cu ion which is blue. But the yellow lead iodide solution and the brown ferric thiocyanate solution lose their color on dilution.

[4] There are three kinds of ions: (1) the colored ion, the combinations of which are always colored regardless of what ions are combined with it, (2) the ion with latent color, which in combination with other ions of latent color may produce colored molecules, but in the free form is colorless and its combinations with ions of the third kind are colorless, (3) the colorless ion, which forms colorless compounds with other colorless ions and with ions which have only latent color.

[5] *Naturwissenschaften,* 11, 167 (1923). This very important paper had appeared in the same year but before our paper. Fajans says in it that for the detection of proper color (Eigenfarbe) one must observe the fluoride, the sulfate or the perchlorate and that anhydrous Cu^{II}, Fe^{II} and Fe^{III} are colorless. As a rule the anhydrous fluorides, sulfates and perchlorates of any metal have the same color as the anhydrous ion of that metal.

[6] *Z. Elektrochem.*, 29, 495 (1923). See also *Z. Physik*, 23, 1 (1924). See also Meisenheimer, *Z. physik. Chem.*, 97, 304 (1921).

[7] FeF_3 is colorless, because Fe^{III} has only latent color and F has no color at all. $FeCl_3$ is yellow, because both ions have latent color. The Fe ion has already deformed the electronic shells of the chloride ions. $FeBr_3$ is dark brown on account of the stronger latent color of the bromide ion. Its electronic shell is badly pulled out of shape by the iron. If we try to make FeI_3, the iron not only deforms the electronic shells of the iodide ion, but it removes one electron completely. The iodine becomes neutral (elementary iodine), and the iron bivalent. (See Fajans, especially his work on refraction and deformability of the electronic shells.)

Summary

The (hydrated) tervalent titanium ion is colorless, but it has a strong latent color, on account of which titanium trichloride is colored.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE ENTROPY OF AQUEOUS IONS

BY WENDELL M. LATIMER AND RALPH M. BUFFINGTON

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A knowledge of the values of the entropies of aqueous ions would place at our command a powerful tool for the direct solution of a large number of thermodynamical problems, many of which otherwise are open only to the most roundabout methods of attack. The treatment of these fundamental entropies has long been deferred by workers in the field of thermodynamics, in part because of the large discrepancies existing in the experimental reaction heats that are involved in their calculation, and in part because of the general lack of information in regard to the entropies of compounds. It would seem, however, that a profitable start may now be made, using as a guide the approximate proportionality pointed out by Latimer[1] between the entropy of solution and the heat of solution of gaseous ions. It is the purpose of this paper to investigate this relation and to give from a survey of existing data a table of values for the entropies of the more important ions. A few typical examples will be given to illustrate the tremendous value of such a table of entropies in the simplification of the thermodynamics of solutions.

As a standard state for comparison we will adopt the hypothetical one molal solution, and define it as a one molal solution of the ions obeying the laws of the perfect dilute solution and the ions possessing the same partial molal heat content that they have at infinite dilution.

In our initial calculations we have no means of obtaining absolute values for the entropies of the individual ions, but must calculate the values as the sum of the entropies of equivalent weights of two ions of unlike charge, or the difference in the entropies of equivalent weights of two ions of like charge.

The sum of the entropies of two ions is most accurately determined from a knowledge of the entropy of a compound and the entropy change for the reaction; compound equals ions *in hypothetical one molal aqueous solution*. For example, the sum of the entropies of H^+ and Cl^- is equal to the entropy of hydrogen chloride plus the entropy of solution of hydrogen chloride. This latter quantity is obtained from the relation $\Delta S = (\Delta H - \Delta F)T$, where ΔH is the heat of solution of hydrogen chloride in an infinitely dilute

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[1] Latimer, THIS JOURNAL, 48, 1234 (1926).

solution, ΔF is the free energy of solution at a concentration of hypothetical one molal hydrogen and chloride ions, and T is the absolute temperature. The data and results of a large number of such calculations have been summarized in Table I.

The sum of the entropies of two ions may also be obtained from the value for the entropy of formation of the ions at hypothetical one molal concentration from their elements, together with the values for the entropies of the elements. In general, the heats of these reactions are large, and are not known with great accuracy. As a consequence the method is not so reliable as the first outlined, and has been employed only in cases where no other data exist, or where the data seemed unusually good. The results are given in Table II.

The difference of the entropies of two ions may be obtained from many types of replacement reactions. Thus the entropy change in the reaction $\text{Na} + \text{H}^+ = \text{Na}^+ + {}^1/_2\text{H}_2$, is again equal to $(\Delta H - \Delta F)/T$, where ΔH is the heat of solution of sodium in a dilute solution of hydrogen ion, and ΔF in calories is 23,074 times the difference in the normal electropotential of sodium and hydrogen. This value of ΔS plus the difference in entropy between half a mole of hydrogen gas and sodium metal then gives the difference between sodium and hydrogen ions. The data and results for

TABLE I

THE SUM OF THE ENTROPIES OF PAIRS OF IONS FROM THE ENTROPY OF THEIR COMPOUND AND THE ENTROPY OF SOLUTION AT 25°

	Entropy of subs.	ΔH of soln.	ΔF° of soln.	ΔS° of soln.	Sum of entropies of ions
HCl	+44.5	−17.3	− 8.7	−28.9	+15.6
HBr	47.0	−19.9	−12.0	−26.4	20.6
HI	49.0	−19 2	−12 7	−21.9	27.1
NaCl	18.5	+ 1.0	− 2.2	+10.6	29.1
KCl	19.7	4.4	− 0.9	18 0	37.7
AgCl	24.0	16.0	+13.3	9.0	33.0
AgBr	25 0	20.1	16.6	11.8	36.8
AgI	26.8	26.4	21.8	15.6	42.4
TlCl	24.6	10.1	5.0	17.2	41.8
TlBr	27.0	13.7	7.4	21.2	48.2
TlI	28.5	17.3	9.9	24.7	53.2
$PbCl_2$	34.4	6.8	7.0	− 0.7	33.7
$PbBr_2$	39.7	10.0	7.7	7.7	47.4
PbI_2	41.3	15.9	11.6	14.3	55.5
MgF_2	15.7	− 2.8	10.7	−45.0	−29.3
CaF_2	17.2	+ 2.7	13.9	−37.3	−20.1
PbF_2	22.0	+ 2.2	10.1	−26.3	− 4.3
Tl_2SO_4	52.5	8.3	5.2	+10.3	+67.8
Ag_2SO_4	49.7	4.5	7.3	− 9.3	40.4
$BaSO_4$	38 0	5.6	13.1	−25 0	13.0
$CaCO_3$	22.0	− 2.0	11.0	−43.3	−23.3
H_2O	16.8	+13.4	19.1	−19 0	− 2.2

this and similar calculations are given in Table III. In all of these tables, free energies and heats are given in kilogram calories, and entropies in small calories per degree.

TABLE II

THE SUM OF THE ENTROPIES OF PAIRS OF IONS CALCULATED FROM THE ENTROPY OF FORMATION FROM THEIR ELEMENTS AT 25°

	ΔH	ΔF	ΔS	S_{elements}		$S_{M^{n+}} + nS_{X^-}$
$Cu + Cl_2$	− 62.6	−46.9	− 52	8	51	7
$Cu + Br_2$	− 40.6	−33.2	− 25	8	36	19
$Fe + 3/2Cl_2$	−127.7	−96.8	−104	7	76	−21
$Fe + 3/2Br_2$	− 95.5	−76.0	− 65	7	55	− 3
$Tl + 3/2Br_2$	− 56.4	−27.3	− 98	18	55	−25

TABLE III

ENTROPY CHANGES IN THE REPLACEMENT OF H^+ BY OTHER IONS AT 25°

Ion	ΔH of reaction	ΔF of reaction	ΔS of reaction	S of element	$S_{M^{n+}} - nS_{H^+}$
Li	−66.0	−68.3	7.7	7.6	0.5
Na	−56.8	−62.6	19.3	12.3	16.8
K	−61.5	−67.4	19.9	16.6	21.8
Rb	−60.8	−67.5	22.4	17.4	25.1
Cu	−129.0	−131.9	9.7	10.6	− 9.1
Zn	−36.3	−35.0	− 4.3	9.8	−23.9
Cd	−17.1	−18.3	4.0	11.8	−13.6
Fe	−20.7	−20.3	− 0.1	7.7	−21.8
Sn	− 4.5	− 6.3	6.0	11.2	−12.2

The space allowed does not permit a detailed discussion of the very large number of sources of data utilized in these calculations. A critical study has been made of many of the original articles. The general references used are Landolt-Börnstein, "Tabellen;" Thomsen, "Thermochemistry;"[2] Lewis and Randall, "Thermodynamics."[3] Special reference should be made to Richards[4] and co-workers' careful work upon the heats of solution of metals in hydrochloric acid. We are indebted to Mr. T. F. McCormick of this Laboratory for experimental data enabling us to correct Richards' values to infinite dilution. Latimer's[5] expression for the entropy of solids has been used in estimating the entropies of certain of the salts. The entropies of hydrogen chloride, hydrogen bromide, hydrogen iodide and chlorine have been taken in general agreement with the Tetrode[6] equation. The value of Latimer and Hoenshel[7] for the

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[2] Thomsen, "Thermochemistry," Longmans, Green and Co., New York, 1908.

[3] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923.

[4] (a) Richards and Burgess, THIS JOURNAL, 32, 431 (1910). (b) Richards and Tamaru, *ibid.*, 44, 1060 (1922).

[5] Latimer, *ibid.*, 43, 818 (1921).

[6] Tetrode, *Ann. Physik*, 33, 434 (1912).

[7] Latimer and Hoenshel, THIS JOURNAL, 48, 19 (1926).

entropy of liquid bromine has been used. Reference should also be made to the "Summary of Electrode Potentials," by Gerke.[8]

Calculation of Relative Ionic Entropies

We may now proceed to use the results of Tables I, II and III to obtain a set of very useful values, namely, the relative entropies of the ions. In so far as the use of the ionic entropies is confined to chemical reactions the absolute values are entirely unnecessary, just as the absolute electrode potentials are quite unnecessary in calculating free energies of reaction. In agreement with the usage of choosing the ionic free energy of hydrogen ion equal to zero in the standard state, we will also take the entropy of hydrogen ion in hypothetical one molal solution equal to zero. The first column of Table IV gives the values of the aqueous entropies in terms of $S_{H^+} = 0$. The second column gives the corresponding values for the ions as monatomic gases calculated from the Sackur equation.[9] Now differences in the entropies of the ions as gases are due entirely to differences in mass and, moreover, it is obvious from the fact that the Trouton constant is independent of mass, that the mass function must be the same

TABLE IV

RELATIVE ENTROPIES OF AQUEOUS IONS AT 25° AND A COMPARISON OF ΔS AND ΔE OF SOLUTION OF GASEOUS IONS

	$S_{H^+} = 0$	S of gas ion	ΔS of solution of gas ion	ΔE of solution of gas ion
Li^+	0.5	31.5	31	119
Ag^+	17.4, 16.2, 15.3	39.7	24	107
Na^+	13.5, 16.8	35.1	20	96
Tl^+	26.2, 27.6, 26 1	41.6	15	78
K^+	22.1, 21.8	36.6	15	77
Rb^+	25.1	39.0	14	72
F^-	−6.0, −4.0	34.5	39	250
Cl^-	15.6	36.4	21	161
Br^-	20.6	38.8	19	140
I^-	27.1	40.1	13	122
Zn^{++}	−23.9	38.3	62	494
Cu^{++}	−24 2, −22 2	38 2	61	475
Fe^{++}	−21.8	37.7	59	465
Sn^{++}	−12.2	39.9	52	465
Mg^{++}	−19.0	35.2	54	450
Cd^{++}	−13.6	39.8	53	440
Ca^{++}	−9 0	36.7	46	379
Pb^{++}	2.4, 6.2, 1.3	41.7	39	345
Ba^{++}	4.0	40.4	36	290
Fe^{+++}	−68, −65	37.7	105	1010
Tl^{+++}	−87	41.6	128	700

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[8] Gerke, *Chem. Rev.*, **1**, 377 (1925).

[9] Lewis, Gibson and Latimer, THIS JOURNAL, **44**, 1008 (1922).

for both liquids and gases. It therefore follows that the entropy of solution of the gaseous ions should be independent of any mass effect and depend only upon the force of attraction between the ions and the water molecules. We should then expect to find a proportionality between the entropy of solution and the energy of solution of the gaseous ions. A comparison of these two values is given in Cols. 3 and 4. The values for the energy of solution are those calculated by Latimer.[1]

A survey of Table IV shows the remarkable parallelism that exists between the entropy of solution and energy of solution, and since it has been shown by the senior author that the energy of solution depends almost entirely upon the size and charge of the ion, we may state that *the entropy of solution of the gaseous ions is also to a high degree a function solely of the size and charge of the ion.* The parallelism is so close that we feel confident that if we had the absolute values for the entropies of the aqueous ions a general relation would be obtained covering all the different ion types. We might now proceed to estimate the absolute values of the ions by choosing a value that would make ΔS and ΔE proportional for both the positive and negative univalent ions. This was done by Latimer[1] in order to obtain roughly the absolute values for the entropies of the electrode reactions. However, since we have no check at present upon the ΔE values for the negative ions it seems more desirable for the purpose of this paper to keep the ΔS in terms of $S_{\mathrm{H}^+} = 0$ and consider the different types of ions separately.

In Figs. 1 and 2 we have plotted the ΔS of solution against the reciprocal of the atomic radii in Ångström units as given by Bragg and Bragg.[10] These curves may be used to estimate the entropy of solution of any uni- or bivalent positive ion whose atomic radius is known, and hence by means of the Sackur equation to obtain the entropy of the aqueous ion; thus, $S_{\text{aq. ion, 298°K.}} = 3/2R\ ln$ at. wt. $+ 25.7 - \Delta S_{\text{solution}}$, where ΔS has the value from Curves I and II, $\Delta S_{M^+} = -12.6 + 58.6(1/r)$ and $\Delta S_{M^{++}} = -9.5 + 94.5(1/r)$.

Hydrogen ion, $\Delta S = 26$ and $\Delta E = 240$, is not in good agreement with the other univalent ions, the value for the entropy of hydrogen ion being proportionally too high. The experimental data used in calculating the entropy of lithium ion are not very reliable, and this value may be several units too low. If more weight were given to hydrogen ion and less to lithium ion the slope of the curve for the univalent ions would be more nearly half that of the bivalent ions, although it is not obvious from a theoretical standpoint what this ratio should be. Of the two values for the tervalent positive ions, that for ferric should be more reliable than the one for thallic, since we obtain a good check between the reactions with iron and both chlorine and bromine carried out by different observers.

[10] Bragg and Bragg, "X-Rays and Crystal Structure," Bell and Sons, London, 1924.

However, we do not feel warranted in drawing any definite conclusions in regard to the tervalent ions, especially since we have very little information regarding the size of ferric and thallic ions in their compounds. The dependence of the entropy on the ionic radius, as shown by Curves 1 and 2, is in general so remarkable that much added weight is given to the belief that in dilute solutions specific hydration effects do not exist, and that the chemical properties of these solutions are those simply of a charged sphere of a given size in a medium of a certain dielectric constant.

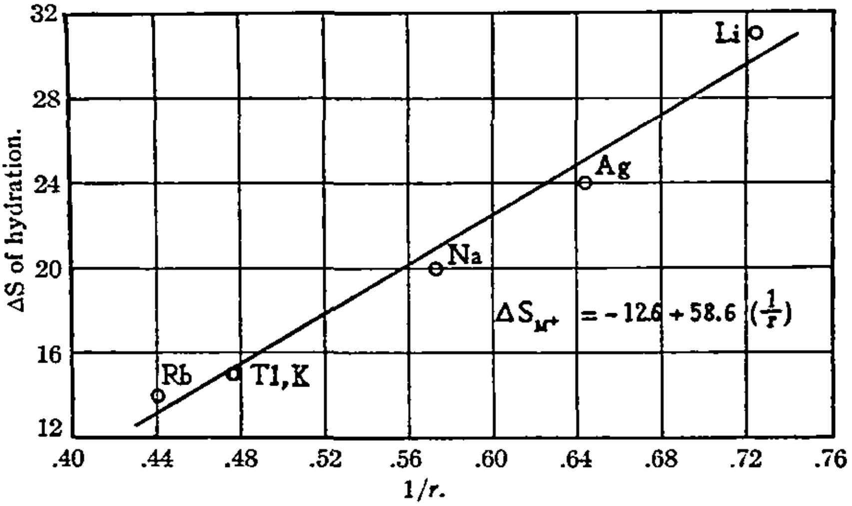

Fig. 1.—Entropy of hydration of univalent gas ions.

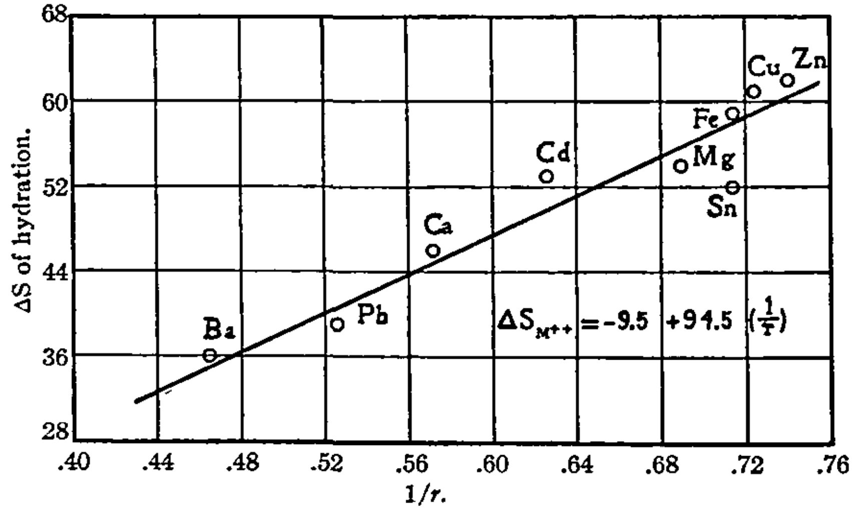

Fig. 2.—Entropy of hydration of bivalent gas ions.

Entropy of Sulfate, Carbonate and Hydroxide Ions

From the data contained in Table I, together with the values for the relative entropies given in Table IV, we may calculate the values referred to hydrogen for sulfate, carbonate and hydroxide ions. Thus for $S_{SO_4^{--}}$ we find 10 entropy units from the data on thallous sulfate and 9 from silver sulfate. This value we have used to obtain the entropy of barium from barium sulfate. From the sum of the carbonate and calcium ions equal to —23, we find for the carbonate ion —14, and from the data on the dissociation of water the entropy of hydroxide ion is —2.

The Use of Ionic Entropies in Thermodynamical Calculations

A large number of thermodynamical calculations using the values of the ionic entropies at once suggest themselves, and a few will be given as typical examples.

The Potential of the Normal Magnesium Electrode.—Richards[11] gives for the heat of solution of "a mole of magnesium in dilute hydrochloric acid, and 200 moles of water at 20°," 110.2 kg. cal. This value probably does not differ from the heat of solution at 25° in infinitely dilute hydrochloric acid by more than 0.2 kg. cal. For the ΔS of the reaction we find 2.1, using for the entropies of the substances: magnesium, 8.3; hydrogen ion, 0; magnesium ion, —19; hydrogen, 29.4. ΔF is then —110.8 kg. cal., and the hypothetical normal electrode potential, —2.40 volts referred to hydrogen. This value is in approximate agreement with that calculated from thermal data on the fluoride and carbonate. Here we have a case where Thomsen's rule is very nearly true, but only, of course, through the merest chance of the entropies of the products being equal to those of the initial substances.

The Heat of Solution of Cuprous Chloride.—We find no value in the literature for the heat of solution of cuprous chloride. This may be calculated, however, using for the entropies: cuprous chloride, 21.1; cuprous ion, 8; chloride ion, 15.5, and for the solubility product 1×10^{-6}. These give ΔS 2.4, ΔF 8.2 and ΔH of solution 8.9 kg. cal. The value for the entropy of cuprous ion was calculated using 1.38 as the radius of the ion.

The Entropy of Solid Magnesium Hydroxide.—As the values for the entropies of the ions become established with greater accuracy, we may reverse the calculations of Table I and calculate the entropies of compounds with considerable assurance, thus avoiding the difficulties of the determinations of heat capacities at very low temperatures. Very little is known regarding the entropy of solid hydroxides, but we can calculate values that appear very reasonable. Thus for magnesium hydroxide we find ΔH of solution equal to zero from Thomsen and ΔF equal to 14.6, using the solubility product 2×10^{-11}. ΔS then is 49.0, and using S_{OH^-} —2 and $S_{Mg^{++}}$ —19, we find S_{298} for magnesium hydroxide to be 26.0 cal. per degree per mole.

The Free Energy of Solution of Zinc Chloride.—One of the most difficult experimental problems is the determination of the free energy change for a very soluble salt going from the solid to hypothetical one molal solu-

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[11] Richards, This Journal, 32, 431, 1176 (1910).

tion. In many cases it is possible neither to set up a cell capable of giving the free-energy change nor to use the Duhem equation applied to the lowering of the freezing point of the solution, because of the inability to obtain equilibrium between the anhydrous salt and solution. However, a knowledge of the entropy of the ions and the heat of solution of the salt at a low concentration permits an immediate calculation of the free-energy change. Thus for zinc chloride, using the values of the entropies zinc chloride, 31; chloride ion, 15.5^-, zinc ion, —24, we find ΔS to be —24. ΔH is —15.6 kg. cal., so that ΔF of solution at a hypothetical one molal concentration is —22.8 kg. cal.

Reliability of Values for the Ionic Entropies

Attention should be called to the large number of checks that we have obtained upon the values given in Table IV. Thus we have calculated the entropies of sodium and potassium ions both from the solution of the metals in acid and from the solution of their chlorides in water. The former involves the heats of the reactions and the potentials of the sodium and potassium electrodes. The latter involves the determination of the activity of the water from freezing-point lowerings and the use of the Duhem equation for obtaining the activities of the salts, together with data for heats of dilution and partial molal specific heats of the solution. In these cases the agreement that we find between two such different methods, of approach and involving data of great experimental difficulties argues well for the reliability of the values obtained for other ions under far more favorable experimental conditions. The data for chloride, bromide and iodide from the corresponding halogen acids seem especially good. Checks are also obtained upon these values through the concordant results secured when those values are used to calculate the entropies of silver and thallous ions from data on their halides. In general, the values obtained by the method in Table I should be more reliable than those by the other methods, as the heats of the reaction are as a rule very much less. When possible, the calorimetric heats of solution of the sparingly soluble salts have been checked against those calculated from the change in solubility with temperature. Of the values obtained from Table III, the entropies of zinc, cadmium and ferrous ions should be the most accurate, as they are obtained from the heats of solution of the metals in acid by Richards, and well established electrode potentials. We believe that the majority of the values are correct to within two entropy units, that is, approximately 600 cal. or 0.026 volt equivalents at 298°K. This belief seems to be substantiated by the curves of Figs. 1 and 2.

Summary

We have collected in Table V the values that we obtain for the relative entropies of the ions referred to hydrogen at hypothetical one molal con-

TABLE V

IONIC ENTROPIES REFERRED TO $H^+ = 0$ AT HYPOTHETICAL ONE MOLAL CONCENTRATION AND 298°K.

	$S_{1\,M,\,298°}$		$S_{1\,M,\,298°}$		$S_{1\,M,\,298°}$
Li^+	1	Fe^{+++}	−67	I^-	27
F^-	− 5	Cu^{++}	−23	Ba^{++}	4
Na^+	15	Zn^{++}	−24	Tl^+	26.5
Mg^{++}	−19	Br^-	20.5	Tl^{+++}	−87
Cl^-	15.5	Rb^+	25	Pb^{++}	2
K^+	22	Ag^+	16	OH^-	−2
Ca^{++}	− 9	Cd^{++}	−14	CO_3^{--}	−14
Fe^{++}	−22	Sn^{++}	−12	SO_4^{--}	9

centration and 298°K. To these might be added many more estimated from the relation found between the entropy of solution and the ionic radii.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE MEASUREMENT OF COEFFICIENTS OF EXPANSION AT LOW TEMPERATURES

SOME THERMODYNAMIC APPLICATIONS OF EXPANSION DATA

BY RALPH M. BUFFINGTON[1] AND WENDELL M. LATIMER

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This research was undertaken with the purpose of obtaining data on coefficients of thermal expansion of solids at low temperatures which are required for testing theories of the solid state. The mathematical development of such theories involves certain differential coefficients, for example, the various elastic moduli, the specific heat and the coefficient of expansion. The functional relations of these quantities are, therefore, important topics for experimental investigation. While most of the important coefficients have been studied at ordinary temperatures, the experimental difficulties have practically limited quantitative work at low temperatures to measurements of specific heats and of coefficients of expansion, and of a few other properties, such as electrical conductivity, whose relations to the main problem are still obscure.

We have three important principles that indicate the method of attack: the third law of thermodynamics,[2] the quantum theory of specific heats[3] and the approximate constancy of the ratio of the specific heat of a substance to its coefficient of expansion which was discovered by Grüneisen.[4]

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[1] National Research Fellow while a part of this work was done.

[2] Lewis and Gibson, THIS JOURNAL, 42, 1542 (1920).

[3] (a) Einstein, *Ann. Physik*, [4] 22, 180 (1907). (b) Debye, *ibid.*, [4] 39, 789 (1912). (c) Born and Kármán, *Physik. Z.*, 13, 297 (1913); 14, 15 (1913).

[4] Grüneisen, *Ann. Physik*, [4] 26, 211 (1908).

Representing volume by V, absolute temperature by T, pressure by P and entropy by S, classical thermodynamics gives the relation $(\partial V/\partial T)_P = -(\partial S/\partial P)_T$. The third law then requires that the volume coefficient of expansion of a perfect crystal approach zero at low temperatures in order that its entropy may become zero independently of the pressure. The approximate validity of the Grüneisen relation and the known behavior of specific heats satisfactorily confirm the third law, but our data show that expansion measurements at still lower temperatures are required for adequate tests of theories of lattice mechanics, such as those of Grüneisen[4,5] and of Born.[6] Reference should also be made to the much less elaborate, but very suggestive theory of Ornstein and Zernicke.[7] The results of such theoretical discussions are necessarily of doubtful accuracy, but being in fair agreement with the facts as far as known, they may, if used with due caution, prove of considerable value. Thus it will be shown that such a semi-theoretical expression leads to satisfactory values for the entropies of solids.

Apparatus and Method

The expansion measurements were made by a modified Fizeau[8] method, in which the displacement of a system of interference bands gives length changes in terms of the half wave length of light used. A Fizeau apparatus can be made sensitive to 0.01 band, or about 2.7×10^{-7} cm. For the expansion over a 5° interval of a 1cm. sample having a coefficient of 10^{-5}, this corresponds to an error of about 0.5%. The accuracy of nearly all expansion work is, however, limited by other factors, such as temperature control and measurement, mechanical displacements, hysteresis effects and, in some cases, by corrections for the refractive index of air. In order to obtain true differential coefficients, not merely total expansions over long temperature intervals, the methods developed in low-temperature vacuum calorimetry have been applied to the problem, and the instantaneous coefficients of expansion of a number of substances have been found from about 90°K. to 310°K.

In the Fizeau method, plane-polished quartz or glass plates are held apart by a known length of the material to be investigated, the wedge-

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[5] (a) Grüneisen, *Ann. Physik*, [4] **33**, 65 (1910); **39**, 257 (1912); **55**, 371 (1918); **58**, 753 (1919); *Verh. deut. physik. Ges.*, **13**, 426, 491, 836 (1911). (b) Grüneisen and Goens, *Z. Physik*, **26**, 235, 250 (1924); **29**, 141 (1924).

[6] Born, "Dynamik der Kristallgitter," Teubner, Leipzig, 1915; and a second edition, much amplified, Teubner, Leipzig, 1923. See also numerous journal articles.

[7] Ornstein and Zernicke, *Proc. Acad. Sci. Amsterdam*, **19**, 1289, 1295, 1304, 1312 (1917).

[8] (a) Fizeau, *Ann. chim. phys.*, [4] **2**, 143 (1864); **7**, 335 (1866). (b) For various modifications of the fundamental method, see Benoit, *Trav. Mem. Bur. Int.*, **1C**, 1 (1881); **6** (1888). (c) Pulfrich, *Z. Instrumentenk.*, **13**, 365, 401, 437 (1893); **18**, 261 (1898). (d) Valentiner and Wallot, *Ann. Physik*, [4] **46**, 837 (1915).

angle between the plates being adjusted for a difference of about 20 half wave lengths in the separations at opposite sides. When the plates are illuminated by parallel, monochromatic light and viewed from the direction of the source, straight, parallel and equally spaced interference bands appear at the reflecting surfaces. As the supports expand, the wedge angle remains constant and the bands move across the plate; when each band has reached the position formerly occupied by its neighbor, the separation of the plates has changed by half a wave length. An expansion measurement, therefore, consists of determining, for a definite temperature interval, the number of bands which pass a fiducial mark.

The interferometer plates, made by Wm. Gaertner and Company of Chicago, were cut from crystalline quartz, with the reflecting surfaces perpendicular to the optic axis, and plane-polished to 0.05 wave length. The upper plate was cylindrical, 3 cm. in diameter and 1 cm. thick. An angle of 20″ between the faces served to throw light reflected from the upper surface out of the field. The lower plate has a base 3 cm. in diameter, and a central portion an additional 1.035 cm. thick. The upper reflecting surface, 2.2 cm. in diameter, was undercut to leave a step 0.5 cm. wide around the piece, 1.035 cm. below the reflecting surface. This shape provided for measurements of expansion relative to quartz, using an interference path of the order of 0.01 cm., as well as for absolute measurements using a long path. In the relative method, three samples about 1.045 cm. long, plane at one end and bluntly pointed at the other, were evenly spaced around the step, and plates and samples clamped together with light springs. By polishing the points of the samples, the wedge angle between the plates was adjusted to give properly spaced bands. In the absolute method, the lower plate was inverted, and samples about 0.4 cm. long were clamped between the reflecting surfaces. In either case, reflection from the lower surface of the lower plate was prevented by blackening it with India ink, and a number of small spots of India ink were placed on the lower surface of the upper plate to serve as fiducial marks.

When set up, the interference apparatus was placed inside a copper block weighing 2.4 kg. A plate-glass window transmitted light, and shielded the apparatus from heat radiation. The block was then hung by strong silk threads in a steel container.[9] When in use, a Dewar tube was brought up over the container, and small amounts of liquid air were added at short intervals. The temperature of the container was controlled sufficiently well in this way to make liquid baths unnecessary, except above room temperature, in which case water was used. Heat lost to the container was balanced by electrical energy in a coil wound on the block, the input being regulated to maintain the temperature constant to 0.1°. The variable junction and 30 cm. of the leads of a copper-constantan thermocouple

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[9] Gibson and Giauque, This Journal, 45, 98 (1923).

were placed inside the block, and the fixed junction in a Dewar tube of cracked ice. The electromotive force of the couple was read to the nearest microvolt on a White potentiometer. The thermocouple was calibrated against the standard couple of Eastman and Rodebush.[10]

A steel outlet tube 1 cm. in diameter and 1 meter long placed near the edge of the top of the container carried the wires and served as the vacuum lead. A glass line was sealed on with de Khotinsky cement, and the wires were brought out through the cement. A mercury aspirator backed by a Nelson oil pump maintained the pressure below 0.0001 mm. as read on a McLeod gage. The light path was through an axial tube 2.5 cm. in diameter and 14 cm. long. A plate with a hole for the light path was welded on at the top, and the vacuum joint made with a plate-glass window and a rubber gasket impregnated with stopcock grease.

The interference method requires a strong source of monochromatic light; a mercury arc in Pyrex glass was used. The green line can be readily isolated by means of a color filter, and gives excellent interference bands. Ultraviolet radiation was absorbed by the walls of the lamp. Light entered the apparatus vertically. The image of a small portion of the arc was thrown on an adjustable slit which was at one principal focus of a collimating lens of 23 cm. focal length, the reflecting surfaces of the plates being at the other. The edge of a reflecting prism was set parallel to the slit, 4 cm. below it and 0.1 cm. back, so that the cone of light just missed the prism going down, was made parallel by the lens, and on reflection from the plates at a small angle with its former path, struck the prism and was reflected horizontally into a telescope. The apparatus being arranged for auto-collimation, the images of the bands and of the marks on the upper plate were viewed with the telescope focused for infinity. A color filter was interposed between the eye and the telescope whenever desired. The telescope was fitted with a filar micrometer eyepiece whose traveling cross-hairs were set parallel to the bands. As nearly as possible, the light path was enclosed in blackened tubing, thus reducing the general illumination of the field to a satisfactory value.

The steel container, the collimating apparatus and the telescope were mounted separately on the side of a pier, thus giving ample opportunity for adjustment and insuring stability. No vibration from the building, or from the ebullition of the liquid air was discernible in the bands.

The green band system greatly predominates; hence the number of green bands transited as the temperature changed could be counted without use of a color filter. The band width in each system being proportional to the wave length, the appearance of the green bands, as modified by the others, changed sufficiently to permit describing each band as it passed a fiducial mark, and assigning it a serial number. Once the whole tempera-

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[10] Eastman and Rodebush, This Journal, 40, 489 (1918).

ture range had been covered, a band could be identified from its description, and further counting was avoided, except as a check.

The final measurements of band positions were made in monochromatic light, using Wratten filter No. 62 to transmit the green line, 5461 Å. The traveling cross-hairs of the micrometer were set on maximum darkness. Either five consecutive or six alternate bands were measured, setting alternately on the bands and the fiducial marks. The temperature was easily maintained constant to 0.1°, but in order to make certain that band drifts had ceased, the measurements were repeated at ten-minute intervals until satisfactory constancy was shown. The average reading of all the bands was taken for the position of the central band. From this, the position of the fiducial marks and the measured band width, the fraction of a green band to be added to the serial number was determined. The sum denoted by Δ bands$_g$, is the number of green bands displaced between the temperature at which band No. 0 was in the standard position, and the temperature of the measurements.

Measurements in the yellow were often taken, especially when the long interference path was used, as they afford an independent check of the band count. Wratten filter No. 22 was used to transmit the yellow lines 5770 Å. and 5791 Å. The superposition of the two band systems gave more or less blurred maxima whose separation corresponded to the average wave length. When the bands of one system fell exactly in the middle between those of the other, the field was practically uniform and measurements were impossible.

Δ bands$_g$ $\times$ 5461/5781.5 gives the number of yellow bands equivalent to Δ bands$_g$. On subtracting the measured fraction of a yellow band from this number, the fractional part of the result represents the calculated separation of green band No. 0 and the following yellow band. (In case a point at which the field became uniform is included in the interval, then 0.50 band must be added.) This quantity, called the displacement constant, must remain the same for all measurements of a series. Since an error of 1 band in the serial number makes an error of 0.055 band in the displacement constant, the sensitivity of the method (0.01–0.02 band) was ample to check the count.

About every fourth measurement was made at room temperature. The values of Δ bands$_g$ so found, when calculated to a single temperature, usually showed a steady drift, and fixed the corrections to be applied to intermediate data. For all the substances investigated, positive values of Δ bands$_g$ correspond to decreases in length. The length changes, Δl, were then found from the relation $\Delta l = -5.461/2\ \Delta \text{ bands} \times 10^{-5}$. An empirical equation was then found which represented Δl as a function of temperature with an accuracy of about 1%, and the residual Δl's were plotted against temperature. The experimental values of dl/dT were then found at round values of the temperature by adding corresponding values of the derivative of the equation and of the slope of the difference plot. In case the absolute method was used, the coefficient of expansion, α, is given by the relation $\alpha = (1/l_0)(\mathrm{d}l/\mathrm{d}T)$. In case the relative method was used, the expression becomes $\alpha = 1/l_0[(\mathrm{d}l/\mathrm{d}T) + 1.035\ \alpha\text{-quartz}_{11}]$. l_0 has been taken as the length at room temperature in preference to other possible choices, such as the instantaneous value, or that at absolute zero. The values of 1.035 α-quartz$_{11}$ were found by interpolation in Table XI.

Experimental Results

The following tables summarize the experimental results. For each substance one table gives the changes in length and the next the coefficients of expansion. For aluminum, copper, silver and rock salt, the length of changes are for the samples of given length, relative to 1.035 cm. of quartz parallel to the axis; for Pyrex glass and quartz, which were measured by the absolute method, the length changes are calculated for unit length of sample. In each case, all measurements near room temperature were used to fix the drift corrections and, therefore, appear as a single one.

Aluminum.—The measurements were made on samples turned from hand-rolled aluminum rod. The behavior was satisfactory. Corrections were readily made for the drift, which totaled 0.5% of the largest expansion. The band count was checked by the indirect method in nearly every case. The regularity of the points on the difference plot gave further evidence that no gross errors were made, and showed that the expansion of the samples was reproducible.

TABLE I

RELATIVE EXPANSIONS OF 1.0456 CM. OF ALUMINUM

T	$-\Delta l \times 10^5$	T	$-\Delta l \times 10^5$	T	$-\Delta l \times 10^5$
315.3	23.6	269 2	96.8	115.9	314.6
314.5	24.9	239.3	143.6	114.5	315.6
310.7	30 9	226.5	162.9	98.1	331.8
297.0	52.7	196.5	208.0	89.3	339.5
276.4	85.5	158.9	261.1	86.5	341.6
273 9	89.4	124.7	304.3		

TABLE II

COEFFICIENTS OF EXPANSION OF ALUMINUM

T	$\alpha \times 10^5$	T	$\alpha \times 10^5$	T	$\alpha \times 10^5$
85	0.881	150	1.693	270	2.199
90	1.020	170	1.815	297	2.275
100	1.187	190	1.917	315	2.319
110	1.323	210	2.000		
130	1.539	240	2.107		

Copper.—The samples were turned from hard-rolled copper rod. The behavior was satisfactory, and no appreciable drift occurred. Green bands only were measured; the band count was verified by repetition. An accident prevented measurements from being made at the lowest temperatures.

Table III

Relative Expansions of 1.0450 Cm. of Copper

T	$-\Delta l \times 10^5$	T	$-\Delta l \times 10^5$	T	$-\Delta l \times 10^5$
312.0	10.7	285.0	36.9	198.9	121.5
310.9	12.0	261.4	60.0	170.8	149.6
304.0	18.5	237.8	82.9	139.4	179.9
295.0	27.0	223.5	96.9	108.6	206.8

Table IV

Coefficients of Expansion of Copper

T	$\alpha \times 10^5$	T	$\alpha \times 10^5$	T	$\alpha \times 10^5$
120	1.203	200	1.513	280	1.648
140	1.290	220	1.538	295	1.679
160	1.384	240	1.564	310	1.699
180	1.459	260	1.606		

Silver.—The samples were turned from a silver rod that had been cast in graphite and hammered. The measurements at room temperature showed complete absence of drift. This was fortunate, as accidents twice caused displacements of several bands. Green bands only were measured, the band count being verified by repetition.

Table V

Relative Expansions of 1.0425 Cm. of Silver

T	$-\Delta l \times 10^5$	T	$-\Delta l \times 10^5$	T	$-\Delta l \times 10^5$
310.3	18.5	260.3	78.7	189.0	155.4
306.3	23.5	250.0	91.3	179.7	180.1
295.0	36.9	241.9	101.3	134.9	237.2
280.1	54.6	228.9	117.6	101.2	279.3
277.2	57.8	228.3	118.3	92.4	289.8
274.3	61.4	212.1	138.7	86.8	296.2
267.8	69.5	211.6	139.3		
265.4	72.1	192.7	163.5		

Table VI

Coefficients of Expansion of Silver

T	$\alpha \times 10^5$	T	$\alpha \times 10^5$	T	$\alpha \times 10^5$
90	1.406	180	1.732	270	1.864
110	1.501	210	1.785	298	1.896
130	1.606	240	1.823	310	1.908
150	1.666				

Sodium Chloride.—Samples cut from a specimen of rock salt proved to have sufficient mechanical strength. Corrections were made in the usual way for the drift, which amounted to 1% of the largest expansion. The band count was checked by the indirect method in almost all cases. The experimental conditions were unusually favorable and there is every reason to believe that very high accuracy was attained.

TABLE VII

RELATIVE EXPANSIONS OF 1.0667 CM. OF ROCK SALT

T	$-\Delta l \times 10^5$	T	$-\Delta l \times 10^5$	T	$-\Delta l \times 10^5$
310.3	25.1	218.0	337.2	127.7	616.1
304.6	44.6	209.5	365.6	126.7	618.7
295.0	78.1	207.9	370.5	103.9	678.0
277.8	137.4	192.0	421.1	103.5	678.6
262.4	189.5	187.7	436.1	94.4	697.5
252.4	223.7	169.6	490.6	85.8	720.1
240.2	264.6	155.2	536.2	85.4	719.6
239.8	265.6	145.5	565.0		
234.0	284.2	138.4	585.5		

TABLE VIII

COEFFICIENTS OF EXPANSION OF ROCK SALT

T	$\alpha \times 10^5$	T	$\alpha \times 10^5$	T	$\alpha \times 10^5$
85	2.278	180	3.478	280	3.916
100	2.537	200	3.543	300	3.986
120	2.843	220	3.641	310	4.016
140	3.103	240	3.742		
160	3.294	260	3.834		

Pyrex Glass.—Measurements of the expansion of Pyrex glass, although of no great theoretical interest, were important to us because we wished to use it in a hydrogen thermometer. Further, because of its low coefficient, it was well adapted for use in testing out the absolute method. The sample was a ring cut from 2.3 cm. tubing, and finished to give three-point support at each end. Both green and yellow bands were measured, and satisfactory checks obtained. The data, however, showed the marked lack of reproducibility long known to be characteristic of glasses. The measurements given in Table IX were chosen from about 35 to give the smooth curve which best represented all the data, and probably largely averaged out the lag in expansion. Unless the expansions of other lots differ from these by more than 5%, which is unlikely, they are amply accurate for the purpose for which they were required.

TABLE IX

TOTAL EXPANSIONS PER CM. AND AVERAGE COEFFICIENTS OF EXPANSION OF PYREX GLASS *G* 702—*EJ*

T	$-\Delta l \times 10^5/l^{25}$	Mean T	$\frac{1}{l_0}\frac{\Delta l \times 10^5}{\Delta T}$
315.9	− 6.6	307	0.37
298.0	0.0	273	.34
248.9	16.9	233	.32
218.3	26.6	202	.29
185.1	36.4	158	.24
130.4	49.4	121	.17
111.8	52.5	99	.11
86.7	55.3		

Quartz, Parallel to the Optic Axis; the Expansion of the Reference.—Absolute measurements of the expansion of quartz were necessary for the calculation of the data relative to quartz. A plate 0.4 cm. thick was cut from a crystal and plane-polished. This and the lower interferometer plate were examined by Dr. Hulin of the Geology Department of the University of California, who reported that both were cut perpendicular to the axis within a possible error of 1°, which was within the limits of permissible deviation. Three cylinders 0.3 cm. in diameter were cut from the plate. One end of each sample was polished to an ellipsoidal surface, and the other was left plane. The final lengths averaged 0.3965 cm. A maximum difference of 0.1 band was found between two series; the difference curve was drawn to average them.

TABLE X

EXPANSIONS OF QUARTZ, PARALLEL TO THE OPTIC AXIS, PER CM.

T	$-\frac{\Delta l}{l_0} \times 10^6$	T	$-\frac{\Delta l}{l_0} \times 10^6$	T	$-\frac{\Delta l}{l_0} \times 10^6$
317.9	1.1	229.7	63.7	123.3	117.1
309.2	8.0	225.3	65.9	122.7	117.3
303.8	12.3	202.1	79.3	114.9	119.6
295.0	18.7	193.7	84.6	108.5	122.1
272.3	35.6	174.2	93.9	95.3	126.4
271.6	35.7	157.4	103.0	85.7	128.7
267.4	38.6	137.8	110.5	85.2	128.7
252.4	49.2	136.4	111.1		
240.0	56.7	136.4	111.8		

TABLE XI

THE COEFFICIENT OF EXPANSION OF QUARTZ PARALLEL TO THE OPTIC AXIS AND dl/dT FOR THE REFERENCE

T	$\alpha \times 10^6$	$1.035\alpha \times 10^6$	T	$\alpha \times 10^6$	$1.035\alpha \times 10^6$
85	0.240	0.248	210	0.574	0.594
90	.267	.276	220	.595	.616
100	.305	.316	230	.616	.638
110	.338	.350	240	.637	.659
120	.369	.382	250	.658	.681
130	.396	.410	260	.679	.703
140	.420	.435	270	.700	.725
150	.444	.459	280	.722	.747
160	.466	.483	290	.743	.769
170	.489	.506	300	.764	.791
180	.511	.528	310	.785	.812
190	.531	.550	320	.806	.834
200	.553	.572			

Discussion

Errors.—The experimental checks secured make it reasonably certain that the whole number of bands was in every case correct. The original direct count was always verified by repetition and, except in the measurements on copper and silver, by the indirect method also. Errors due to permanent displacements of any character were reduced to the order of 0.02 band by the drift correction. The regularity of the points on the difference plots indicated that individual measurements at low temperatures could be reproduced with an accuracy of 0.1 to 0.2 band. Temperature equilibrium was definitely established in every experiment, the drift amounting to only a few hundredths of a band per hour. True lag in the expansion is a possible explanation of some of the discrepancies; in the case of Pyrex glass it was evidently the controlling factor. Probably the real explanation of the usual errors lies in the finite size of the slit, in conjunction with small displacements of the optical system. The difference plot indicated that the probable errors in the measurements on the 0.3965cm. sample of quartz were about 0.03 band, making the equivalent error in the expansion of the reference about 0.08 band. The probable error of an individual relative measurement, including the error in the reference, is estimated as 0.25 band, or 0.5×10^{-5} cm. The use of sensitive difference plots in the final calculations of the coefficients of expansion greatly reduced the effect of these accidental errors. The temperature scale is the only important source of systematic error of which we are aware. On the basis of unfinished work with a hydrogen thermometer, the errors of the scale are judged to be of the order of 0.2°; and of the size of the degree, never more than 1%. This may cause a maximum error of 1% in the coefficients of expansion without, however, greatly affecting the length changes.

Previous Work

Metals.—Recent experimental papers by Souder[11] and by Hidnert[12] have included discussions of previous data for aluminum and copper which need not be repeated here. These papers are particularly important in that the authors systematically attack the problem of the relations of composition and heat treatment to expansion. Our work is in good general agreement with that of other observers, especially at room temperature. Although the low-temperature data of Ayers[13] and of Shearer[14] on aluminum and of Dorsey[15] on copper scatter somewhat, they can be represented fairly well by the graph of our own data. Discrepancies are also found in the case of silver. Our results are 1 to 2% lower than those of Dorsey over most of the range; the room-temperature data summarized in the Landolt-Börnstein "Tabellen" also show considerable variations. It is,

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[11] Souder and Hidnert, *Sci. Pap. Bur. Stand.*, **17**, 497 (No. 426) (1922); **17**, 611 (No. 433) (1922).

[12] Hidnert, *ibid.*, **17**, 91 (No. 410) (1922).

[13] Ayers, *Phys. Rev.*, **20**, 38 (1904).

[14] Shearer, *ibid.*, **20**, 52 (1904).

[15] Dorsey, *ibid.*, **25**, 88 (1907).

perhaps, useless to expect better agreement among the results for metals, as specific-heat measurements also show variations; accurate values for the coefficient of expansion of particular samples, over a wide range of temperatures, are nevertheless significant.

Rock Salt.—Very few rock-salt data are available for comparison. Fizeau[16] found $\alpha = 4.040 \times 10^{-4}$ at 40°, in agreement with the present work. A recent paper by Henglein[17] gives values based on specific-gravity measurements at the temperatures of ice, carbon dioxide and liquid air which agree with our own within the errors of her method.

Quartz.—There are many excellent data in the literature for the expansion of quartz above the ice point, but it is difficult to choose a fair method of comparing them with our own for the reason that the temperature ranges do not overlap sufficiently. Nearly all observers have expressed their results by means of equations of the type $\alpha = a + bt$, where t is the Centigrade temperature. If $d\alpha/dT$ is really a function of temperature, the values found for a and b will depend on the range covered by the measurements; $d\alpha/dt$ evidently decreases slightly with increasing temperature, resulting in larger values of a and smaller values of b than the data at higher temperatures. The differences found do not cast doubt on the assumption that the expansion of all samples is identical. For purposes of comparison, we have collected in Table XII the values $(d\alpha/dT)_{273.1}$, $\alpha_{273.1}$ and $\alpha_{298.1}$, as given by the linear equations, and have added values estimated from Dorsey's table, Scheel's values from the equation $\alpha =$

TABLE XII

COMPARISON OF THE DATA FOR THE EXPANSION OF QUARTZ PARALLEL TO THE AXIS AT 273.1° AND 298.1°

Author	$\left(\frac{d\alpha}{dT}\right)_{273.1} \times 10^5$	$\alpha \times 10^5_{273.1}$	$\alpha \times 10^5_{298.1}$
Fizeau[a]	0.001770	0.710	0.754
Benoit[b]	.001602	.716	.756
Reimerdes[c]	.001638	.6925	.7334
Bein[d]	.001616	.71525	.7557
Scheel (1°)[e]	.001630	.7144	.7551
Scheel (2°)[f]	.001877	.7085	.7541
Dorsey[g]	(.0022)	.7542	(.80)
Buffington and Latimer	.002111	.7069	.7597

[a] Fizeau, *Compt. rend.*, **62**, 1101, 1133 (1866); *Pogg. Ann.*, **128**, 564 (1866).

[b] See Ref. 8b.

[c] Reimerdes, *Inaugural Dissertation*, Jena, 1898.

[d] Bein, *Verh. deut. physik. Ges.*, **14**, 1997 (1912).

[e] Scheel (1°), *Ann. Physik*, [4] **9**, 837 (1902).

[f] Scheel (2°), *Ber. physik. Ges.*, **5**, 3 (1907).

[g] Dorsey, *Phys Rev.*, **27**, 1 (1908).

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[16] Fizeau, *Compt. rend.*, **64**, 314 (1867).

[17] Henglein, *Z. physik. Chem.*, **115**, 91 (1925).

$(0.7085 + 0.001877t - 0.00000216t^2) \times 10^{-5}$, and our own, calculated from the equation that holds from $T = 170°$ to $310°$, $\alpha = (0.1304 + 0.002111T) \times 15^{-5}$. Dorsey's values at low temperatures are higher than our own. This may have been due to an error in cutting his samples, as the coefficient perpendicular to the axis is large. Scheel gives 107.4×10^{-5} for $\Delta l/l_0$ between —190° and 16°, as against 106.2×15^{-5} calculated from our data.

Applications

The Third Law of Thermodynamics.—The present statement of the third law requires that the coefficient of expansion of a perfect crystalline solid approach zero at absolute zero. In the absence of expansion data at very low temperatures, some method of extrapolation must be devised in order to check the prediction. An indirect method due to Grüneisen has proved the most satisfactory.

The ratio of the specific heat of a substance to its volume coefficient of expansion gives the relation of energy input to volume change. The discovery by Grüneisen, already referred to, that this ratio is nearly independent of temperature, marked a great advance in our knowledge of the solid state, and at the same time strengthened the position of the third law.

Of the substances investigated, aluminum, copper, silver and sodium chloride are isotropic crystalline solids whose specific heats fall on the Debye[3b,18] curve. Table XIII indicates the calculation of $C_p/3\alpha$ for these substances at various temperatures. The values of C_p were read from graphs prepared by Lewis and Gibson, and by Lewis, Gibson and Latimer[19] in their calculation of entropies; references to the original data are given in their papers. The trend of the $C_p/3\alpha$ values gives a very satisfactory confirmation of the third law, as in each case α increases slightly more rapidly with the temperature than does C_p. The limiting values of $C_p/3\alpha$ at absolute zero might be guessed from these results, but it is unnecessary for our purpose. The necessity of limiting the third law to

TABLE XIII

CALCULATIONS OF $C_p/3\alpha$

	T	C_p	$\alpha \times 10^5$	$\frac{C_p \times 10^{-4}}{3\alpha}$		T	C_p	$\alpha \times 10^5$	$\frac{C_p \times 10^{-4}}{3\alpha}$
Al	100	3.10	1.185	8.72	Ag	100	4.85	1.450	11.26
	160	4.62	1.758	8.76		160	5.63	1.694	11.08
	220	5.31	2.042	8 67		220	5.91	1.800	10.94
	280	5.70	2.223	8 55		280	6.02	1.876	10.70
Cu	100	3.90	(1.10)	(11.8)	$^1/_2$NaCl	100	4.29	2.537	5.64
	160	5.13	1.385	12.34		160	5.24	3.294	5.30
	220	5.55	1.540	12.01		220	5.59	3.641	5.12
	280	5.78	1.650	11.68		280	5 77	3.916	4.91

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[18] Lewis and Gibson, THIS JOURNAL, 39, 2554 (1917).

[19] Lewis, Gibson and Latimer, *ibid.*, **44**, 1008 (1922).

crystalline solids is well illustrated by expansion data; quartz glass and supercooled silicon have negative coefficients of expansion at low temperatures, and we suspect that Pyrex glass has also.

Interatomic Constraints and Entropy.—It appears quite probable, on *a priori* grounds, that V and $C_p/3\alpha$ might be used to introduce into the entropy equation for solids[20] terms that depend on the constraints between atoms. To do this we shall make use of an expression for the frequency of vibration of the atoms of a solid considered as resonators. According to Grüneisen,[21]

$$\nu = M^{-\frac{1}{2}} \cdot V^{\frac{1}{3}} \cdot \left(\frac{C_v}{3\alpha}\right)_{T=0} \times \text{constant} \qquad (1)$$

where M is the atomic weight and V the volume per gram atom. Combining with Planck's equation for the entropy of a system of resonators,

$$S_v = NR\, ln \frac{kT}{h\nu} + \text{constant} \qquad (2)$$

where S_v is the entropy of one mole at constant volume, N is the number of degrees of freedom, three in our case, k is the gas constant per molecule and R per mole, and h is Planck's constant, we obtain

$$S_v = 3RlnT + 3/2\ RlnM + RlnV - 3/2\ Rln\ (C_v/3\alpha)_{T=0} + \text{constant} \qquad (3)$$

It is interesting to note that for a perfect monatomic gas, Equation 3 reduces to the well-known Sackur equation[22]

$$S = 3/2\ RlnT + 3/2\ RlnM + RlnV + \text{constant} \qquad (4)$$

Equation 1 was derived by Grüneisen for an "ideal" monatomic solid whose specific heat has reached the equipartition value; probably no real substance fulfils the conditions imposed. Equation 3, therefore, merely qualitatively indicates the form of the relations to be expected. In order to get a simpler basis for comparison of different substances, it is convenient to make arbitrarily a few minor changes in Equation 3. S_p is substituted for S_v, as it is of far greater practical importance, and differs from the latter by only about 0.2 unit in ordinary cases. $(C_p/3\alpha)_{T=160}$ is substituted for $(C_v/3\alpha)_{T=0}$ in order to avoid uncertain extrapolations. As the calculations are made for $T = 298.1$, $3/2RlnT$ is included in the constant term. Equation 3 is then replaced by

$$S_{p,\,298} = 3/2RlnM + RlnV - 3/2Rln\ (C_p/3\alpha)_{T=160} + 26.5 \qquad (5)$$

where the additive constant has been evaluated from the data on aluminum, copper and silver as indicated in Table XIV. The values of $S_{p,\,298}$ are taken from the table of Lewis, Gibson and Latimer.[19] The table includes calculations of the constant based on Grüneisen's values of $C_v/3\alpha$ for magnesium, iridium and lead. The agreement is satisfactory, as these $C_v/3\alpha$ values are very rough.[23]

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[20] Latimer, THIS JOURNAL, 43, 818 (1921).

[21] Gruneisen, *Ann. Physik,* [4] 39, 293 (1912).

[22] Sackur, *Ann. Physik,* [4] 36, 598 (1911); 40, 67 (1913).

[23] Ref. 21, p. 294.

TABLE XIV

EVALUATION OF THE CONSTANT OF EQUATION 5

	M	V	$\frac{C_p \times 10^{-4}}{3\alpha}$	$S_{p,\,298}$	Constant
Al	26.97	10.00	8.76	6.82	26.34
Cu	63.57	7.10	12.34	8.18	26.84
Ag	107.88	10.27	11.08	10.25	26.28
Mg	24.32	14.00	8.1	8.3	27.2
Ir	193.1	8.61	32.1	8.7	26.5
Pb	207.2	18.27	8.0	15.53	27.5

Possibilities for the extension of the scope of Equation 5 at once suggest themselves; certain limitations are, however, obvious. The specific heat must have approximately reached the equipartition value; non-crystalline substances must be excluded as they deviate widely from the Grüneisen relation. Binary compounds crystallizing in the regular system appear to offer the best chance. The data are very fragmentary; sodium chloride appears to be the only substance fulfilling the conditions for which all the data are available. By assuming that $C_p/3\alpha$ for potassium chloride and lead sulfide changes in about the same way as for the substances given in Table XIII, it is possible to make an approximate calculation for these also.

It is necessary to replace M in Equation 5 by some other mass function. Latimer[20] has shown that in solid compounds whose specific heats have reached the equipartition value, the mass contribution of each element is $3/2 R \ln M$ per gram atom. The required function is, therefore, the geometric mean of the atomic weights, as V and C_p are taken per gram atom. For binary compounds Equation 5 becomes

$$S_{p,\,298} = 3/2 R \ln \sqrt{M \cdot M'} + R \ln V - \frac{3}{2} R \ln \left(\frac{C_p}{3\alpha}\right)_{T=160} + 26.5 \qquad (6)$$

where $S_{p,\,298}$ is evidently the entropy per gram atom.

The results of the calculations are summarized in Table XV. The check obtained for sodium chloride is regarded as particularly significant. Unfortunately, there are insufficient data to permit similar calculations for substances crystallizing in other systems.

TABLE XV

ENTROPIES OF SALTS ACCORDING TO EQUATION 6

	$\left(\frac{C_p \times 10^{-4}}{3\alpha}\right)_{T=160}$	$S_{p,\,298}$ Calcd.	$S_{p,\,298}$ Obs
NaCl	5.30	9.22	8.72 9.25
KCl	6.0	9.8	9.85
PbS	10.7	10.4	11.4

Acknowledgment is due to the Bureau of Standards for a copy of their extensive manuscript bibliography on thermal expansion.

Summary

The instantaneous coefficients of expansion of aluminum, copper, silver, rock salt, quartz parallel to the optic axis, and Pyrex glass have been determined by an interference method for temperatures between 90° and 315°K.

The coefficients of expansion of the crystalline solids approach zero at low temperatures, in agreement with the prediction of the third law of thermodynamics. The coefficients of expansion change slightly more rapidly with temperature than do the specific heats.

Guided by a semi-theoretical expression due to Grüneisen, terms depending on the constraints between atoms are introduced into the equation for the entropy of solids. The entropies of six monatomic solid metals are satisfactorily represented by the equation $S_{p, 298} = 3/2 R \ln M + R \ln V - 3/2 R \ln (C_p/3\alpha)_{T = 160} + 26.5$. A simple extension to binary compounds proves successful.

It is pointed out that data at still lower temperatures are required before adequate tests of theories of lattice mechanics can be made.

Berkeley, California

[Contribution from the Chemical Laboratories of Brown and Stanford Universities]

SOLUTIONS OF THE ELECTRONEGATIVE ELEMENTS IN LIQUID AMMONIA. I. THE ACTION OF SELENIUM, TELLURIUM, ARSENIC AND A SOLUTION OF SULFUR IN LIQUID AMMONIA UPON CYANIDES

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Introduction

Chlorine dissolves readily in water in accordance with the equation, $Cl_2 + HOH \rightleftharpoons HCl + ClOH$. A solution of chlorine in water contains, therefore, in addition to free chlorine, hydrochloric and hypochlorous acids, which contain, in terms of the valence theory respectively, univalent negative and univalent positive chlorine. It is known that liquid ammonia reacts with the halogens in the same manner that water does, although more energetically. Chlorine and bromine, for instance, readily react with liquid ammonia, even at —40°, to form ammonium chloride or bromide and nitrogen gas in the same manner that fluorine reacts with water to give hydrofluoric acid and ozonized oxygen.[2] Iodine is very

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[1] National Research Fellow.

[2] There is evidence for the formation during these reactions of the very unstable chloro- and bromo-amines, the hypochlorous and hypobromous acids of the ammonia system (Franklin, unpublished work).

soluble in a small volume of liquid ammonia, but reacts reversibly with it on dilution in the sense of the equation $I_2 + 2NH_3 \rightleftharpoons INH_2 + NH_4I$ to form iodine-amine or a deammonation product and ammonium iodide.[3] Since the iodine-amine may be regarded as a hypo-iodous acid of the ammonia system,[4] this reaction is entirely analogous to the reaction between chlorine and water.

Ruff and Geisel,[5] Franklin and Kraus,[6] Moissan[7] and others have found that sulfur slowly dissolves in liquid ammonia at ordinary temperatures without evolution of gas. The first two authors have suggested that sulfur reacts with ammonia in the same manner that chlorine reacts with water, perhaps in accordance with the equation

$$10S + 4NH_3 \rightleftharpoons 6H_2S + N_4S_4 \tag{1}$$

for it was found that silver iodide in ammonia solution reacts with dissolved sulfur to give a precipitate of silver sulfide and a solution of sulfur nitride, N_4S_4. Both of the substances on the right-hand side of the equation are combined with the solvent, hydrogen sulfide forming ammonium sulfide and nitrogen sulfide a mixture of the two acids, $S(NH)_2$ and $S_2(NH)_2$, which may be regarded, respectively, as a sulfurous and a thiosulfuric acid of the ammonia system.[4,8] The products of the reaction of sulfur and liquid ammonia therefore contain sulfur in different states of nitridation (oxidation), just as do the products of the action of chlorine on water or of iodine on ammonia. In support of Equation 1, Ruff and Geisel have found that small quantities of ammonium sulfide may be volatilized by passing a current of dry hydrogen through a saturated solution of sulfur in ammonia.[3] Furthermore, hydrogen sulfide and sulfur nitride dissolved in liquid ammonia were found to react to give a solution identical with the solution of elementary sulfur in ammonia.

Some years later, Ruff and Hecht[9] upon examining the freezing-point curve of solutions of sulfur in liquid ammonia found one compound, $S \cdot 6NH_3$, m. p. —78.5°, characterized by a flat maximum and obtained evidence for the existence of $S \cdot 3NH_3$. These authors conclude, therefore, that the previously assumed equilibrium between sulfur nitride and hydrogen sulfide in liquid ammonia, as represented by Equation 1, is of minor importance, as the sulfur for the most part is present in the form of the solvates mentioned above.

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[3] Ruff, *Ber.*, **33**, 3025 (1900). Hugot, *Compt. rend.*, **130**, 505 (1900).

[4] Franklin, This Journal, **46**, 2142 (1924), and unpublished work.

[5] Ruff and Geisel, *Ber.*, **38**, 2659 (1905).

[6] Franklin and Kraus, *Am. Chem. J.*, **20**, 830 (1898).

[7] Moissan, *Compt. rend.*, **132**, 510 (1901).

[8] Sulfur nitride may be regarded as a mixed anammonide of sulfurous and thiosulfuric acids; $N_4S_4 + 2NH_3 = 2S(NH)_2 + S_2(NH)_2$.

[9] Ruff and Hecht, *Z. anorg. Chem.*, **70**, 49 (1911). Hecht, "Dissertation," Danzig, 1911.

Now, certain objections may be raised to the theories of Ruff and Geisel and of Ruff and Hecht in regard to the constitution of solutions of sulfur at temperatures far removed from the freezing point of the solvent. Ammonium monosulfide should not exist in the presence of an excess of sulfur, and indeed the author found that these two substances readily react in liquid ammonia to form very soluble ammonium polysulfides. If sulfur nitride, S_4N_4, is to be regarded as a mixed anammonide of sulfurous and thiosulfuric acid, and if aquosulfurous acid reacts with sulfur to form aquothiosulfuric acid,[9a] one would expect the sulfurous acid part of sulfur nitride to take up additional sulfur, in accordance with the equation $S + S(NH)_2 = S_2(NH)_2$ to form ammonothiosulfuric acid. It was found that sulfur nitride did react very slowly with sulfur solution to form a deep blue solution which, however, appeared to contain in addition some other sulfur acids of the ammonia system.[10] Franklin and Kraus[11] have found that a solution of sulfur in liquid ammonia conducts the electric current as well as many salts in this solvent. It would seem logical that the ions taking part in the conduction process were derived in some such manner as indicated by Equation 1, although it is possible that the sulfur is all in the anion and the cation is some sort of a solvent complex associated with a positive charge.[12] If the latter alternative were true, we should not expect gas to be liberated at either electrode upon electrolysis, for sulfur dissolves in ammonia without evolution of gas, and the solution is not decomposed in the presence of a catalytic surface such as a platinum electrode. Preliminary experiments indicated that nitrogen and hydrogen were liberated during electrolysis of a solution of sulfur in liquid ammonia in such volumes as to indicate very appreciable quantities of dissolved sulfur nitride and ammonium sulfide.[13]

It was with the hope of obtaining further evidence concerning the constitution of solutions of sulfur in ammonia that the present investigation was undertaken. As a first step in the study of the chemical properties of sulfur solutions an investigation has been made of the action upon this solution of a number of metallic cyanides. In conjunction with this work it was of interest to see whether selenium, tellurium and arsenic would react with cyanides in the same manner as sulfur.

[9a] In small amounts only, due to the instability of the free acid. Aloy, *Compt. rend.*, **137**, 51 (1903); *J. Chem. Soc.*, **61**, 199 (1892).

[10] Ruff and Hecht (Ref. 9 p. 55) have obtained evidence for the existence of three compounds formed by the interaction of ammonia solutions of sulfur nitride and sulfur.

[11] Franklin and Kraus, *Am. Chem. J.*, **24**, 89 (1900).

[12] Iodine, iodine mono- and trichloride form conducting solutions in which all of the halogen appears to be in the anion. Bruns, *Z. physik. Chem.*, **118**, 89 (1925). Bruner and Galecki, *ibid.*, **84**, 513 (1913). Bruner and Bekier, *ibid.*, **84**, 570 (1913).

[13] These results will be published at a later date.

Purification of Materials and Manipulation

Selenium and sulfur were prepared as described in a preceding article.[14] Tellurium was purified according to the method of Kraus and Chiu.[15] Arsenic was chemically pure material, the oxide coat of which had been sublimed away by strong heating in a current of ammonia.

The reactions described in this paper were carried out in two-legged glass reaction tubes according to the methods of Franklin.[16] The manipulations may be understood from the description of a typical experiment, in which aluminum selenocyanide was prepared.

Aluminum cyanide was prepared in one leg of a reaction tube by the action of a solution of mercuric cyanide in liquid ammonia upon aluminum wire.[17] The resulting solution of aluminum cyanide was decanted into the other leg of the reaction tube, in which had been placed selenium in excess of the amount theoretically required for the reaction. The leg of the reaction tube containing the residue of amalgamated aluminum was opened, cleaned out and resealed. Into this leg was decanted the solution of aluminum selenocyanate. As this substance was so soluble in ammonia that it could not be purified by crystallization, analyses were made of the crude solid remaining after evaporation of the solvent from the reaction tube.

Thiocyanates were similarly prepared by the action of a solution of sulfur in liquid ammonia upon a cyanide. The soluble cyanides of potassium and aluminum were carefully titrated with sulfur solution so as to obtain a thiocyanate as pure as possible. Magnesium cyanide was used in excess, for it is only slightly soluble in ammonia.

For the purpose of analysis, specimens were treated with water and then with dil. sulfuric acid. Selenocyanates were thus decomposed with the formation of red selenium, hydrocyanic acid and salts of ammonia and the metal present in the specimen. The selenium was removed by filtration and the remainder of the analyses made upon the filtrate. It was generally found that a small additional quantity of selenium could be precipitated from a portion of this filtrate by boiling. It was necessary to remove hydrocyanic acid by precipitation as silver cyanide prior to the determination of ammonia. The sulfuric acid solution of a thiocyanate was treated with silver nitrate to precipitate silver thiocyanate and the remainder of the analyses were made upon the filtrate from this precipitate.

Equilibria in the Solution of Sulfur in Liquid Ammonia

Sulfur solution was found to react very readily with solutions of the cyanides of potassium, aluminum and magnesium in liquid ammonia to give

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[14] Bergstrom, This Journal, 48, 146 (1926).

[15] Kraus and Chiu, *ibid.*, 44, 2001 (1922).

[16] Franklin, *ibid.*, 27, 831 (1905); 29, 1694 (1907); 35, 1460 (1913); 46, 1545 (1924); *J. Phys. Chem.*, 15, 510 (1911); 19, 539 (1915).

[17] Bergstrom, This Journal, 46, 1559 (1924).

the corresponding thiocyanates to the exclusion of appreciable quantities of by-products. It is therefore evident that if a solution of sulfur in liquid ammonia contains sulfur nitride and ammonium sulfide, as the work of Ruff and Geisel would indicate,[3] these two substances must either be capable of reacting separately with cyanide solutions to give thiocyanates or, failing to do this, they must react with one another, in accordance with Equation 1, read from right to left, to give sulfur, which in turn reacts with the cyanides. The following experiments showed the latter alternative to be correct.

A solution of sulfur nitride, N_4S_4, in liquid ammonia was mixed with a solution of aluminum or zinc cyanide in excess in a two-legged reaction tube. At the end of a month the yellow color of the sulfur nitride solution had not appreciably lightened, showing that sulfur nitride was not to any great extent converted to thiocyanate. A solution of ammonium sulfide, prepared by passing dry hydrogen sulfide into liquid ammonia in a reaction tube cooled to —40°, failed to react in a week with aluminum cyanide to form appreciable quantities of thiocyanate. It was found, however, that ammonium polysulfide, prepared by the action of sulfur upon ammonium monosulfide solution, slowly became colorless when poured into a solution of aluminum cyanide. The blue solution resulting from the very slow action of sulfur nitride upon sulfur, reacts with aluminum cyanide to form some thiocyanate and a yellow solution of sulfur nitride. Cyanides, therefore, may react with polysulfide sulfur or with such extra sulfur as may have entered into combination with sulfur nitride, to form thiocyanate, ammonium sulfide and sulfur nitride. These latter two substances then react with each other to form sulfur, which in turn reacts with cyanides to form thiocyanates. When sulfur dissolves in liquid ammonia one is concerned with a number of reactions and equilibria, among which are the following: $10S + 6NH_3 \rightleftharpoons S_4N_4 + 6H_2S$; $H_2S + 2NH_3 = (NH_4)_2S$; $S_4N_4 + 2NH_3 = 2S(NH)_2 + S_2(NH)_2$; $(NH_4)_2S + xS = (NH_4)_2S_{x+1}$; $(NH_4)_2S_{x+1} \rightleftharpoons (NH_4)_2S_x + S$, etc., $S_4N_4 + S \rightleftharpoons$ other sulfur acids of the ammonia system.

From our knowledge of the reactions between sulfur solutions and the cyanides of potassium, magnesium and aluminum, we should expect silver and mercuric cyanides to react with dissolved sulfur to form thiocyanates alone. While some thiocyanate is obtained, silver and mercuric sulfides are precipitated in considerable quantities at the same time and the solution is found to contain sulfur nitride. These reactions may reasonably be interpreted by assuming in solution sulfide ions formed in accordance with Equation 1, read from left to right. That mercuric sulfide is not instantaneously precipitated when sulfur solution is poured into a solution of mercuric cyanide, affords evidence for the existence in solution of ammonium polysulfide, for the mercuric polysulfide first formed may exist for a very short length of time before it decomposes into sulfur and the more stable mercuric monosulfide.

The Action of Selenium, Tellurium and Arsenic on Solutions of Cyanides in Liquid Ammonia

Pure selenium very slowly attacks the elements arsenic, zinc, copper and magnesium and readily reacts with the cyanides of magnesium, aluminum, zinc and potassium to form the corresponding selenocyanates. An excess of selenium was found to precipitate nearly all of the silver from a solution of silver cyanide, the precipitate containing silver selenide and selenium nitride or a silver salt of this substance, while the solution contained ammonium selenocyanate. Mercuric cyanide and selenium react in a similar manner. Obviously, these reactions are closely analogous to the corresponding reactions of a solution of sulfur and one may conclude that selenium has an extremely slight solubility in liquid ammonia, such a solution resembling in its character the solution of sulfur in the same solvent. In other words, selenium tends to react with ammonia to form selenium nitride and ammonium selenide.

Tellurium failed to react with magnesium, arsenic or copper in liquid ammonia, but did dissolve very slowly in solutions of aluminum and potassium cyanides. Evaporation of these solutions to dryness appeared to cause decomposition into cyanide and elementary tellurium. No definite compounds were isolated. Arsenic failed to react with solutions of potassium or aluminum cyanides over a long period of time.

Nitridizing Properties of Sulfur and Selenium

Sodium in liquid ammonia solution precipitates, or reduces silver from a solution of silver iodide just as any element, in general, displaces, or reduces, a less electropositive element from solutions of its salts.[18] In a similar manner sulfur precipitates, or nitridizes (oxidizes), lead from a solution of potassium polyplumbide in liquid ammonia in accordance with the equation, $K_4^{++++}Pb_9^{----} + 2S = 2K_2S + 9Pb$, just as any element, in general, displaces, or nitridizes, a less electronegative element from a solution containing this latter as an anion.[19] The halogens are strong nitridizing or oxidizing agents in reactions that do not involve the replacement of one element by another. Even selenium slowly nitridizes cuprous cyanide in liquid ammonia solution to form a precipitate of cupric selenide and a solution of cupric selenocyanate. Sulfur or selenium precipitates a copper sulfide or selenide from a solution of cuprous thiocyanate in ammonia, at the same time nitridizing a portion of the cuprous salt to the cupric condition. The action of sulfur and selenium upon solu-

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[18] Kraus and Kurtz, This Journal, 47, 54 (1925).

[19] Bergstrom, *ibid.*, 47, 1503 (1925).

tions of cyanides may be regarded as a nitridation, inasmuch as a carbonite of the ammonia system is converted to a mixed thio- or selenocarbonate.[20]

Preparations of Thiocyanates and Selenocyanates

Potassium Thiocyanate.—The reaction between potassium cyanide and sulfur solution is noticeably slower than the reaction between sulfur and the cyanides of magnesium or aluminum, in spite of the low solubility of magnesium cyanide. Calcd. for KSCN: SCN, 59.8. Found: 59.0.

Magnesium Thiocyanate.—Preparation 1. Subs. (20°),[21] 0.4135: (1/1)[22] 0.6687 AgSCN; (1/4) of filtrate from AgSCN, 0.03393 NH_3; (1/2) 0.1110 $Mg_2P_2O_7$.

Preparation 2. Subs. (−33°), 0.7219: (20°) 0.6189, (136°) 0.5479. A portion of the salt liquefied at this temperature. (1/1) 0.9916 AgSCN; (2/5) 0.05324 NH_3; (3/5) 0.2006 $Mg_2P_2O_7$. Calcd. for $Mg(SCN)_2 \cdot 4NH_3$: Mg, 11.7; SCN, 55.7; NH_3, 32.7. Found (20°): Mg, 11.7, 11.8; SCN, 56.6, 56.1; NH_3, 32.8, 33.0.

Aluminum Thiocyanate.—In Preparations 1 and 3 approximately the calculated amount of sulfur was used; in Preparation 2 a slight excess.

Preparation 1. Subs. (20°), 0.5166: (1/1) 0.8903 AgSCN; (1/4) 0.03908 NH_3; (1/2) 0.0490 Al_2O_3.

Preparation 2. Subs. (20°), 0.6476: (77°) 0.5719; (1/4) 0.02813 NH_3; (3/4) 0.0828 Al_2O_3.

Preparation 3. Subs. (30°), 0.9245: (1/4) 0.06864 NH_3; (1/2) 0.0879 Al_2O_3.

Calcd. for $Al(SCN)_3 \cdot 5NH_3$: Al, 9.4; SCN, 60.8; NH_3, 29.7. Found: (20°): Al, 10.0, 9.0, 10.1; SCN, 60.3; NH_3, 30.2, 29.9, 29.7.

Potassium Selenocyanate.—Calcd. for KSeCN: K, 27.1; Se, 54.9. Found (20°): K, 27.6, 27.5; Se, 53.3, 54.5; NH_3, 1.0,—.

Magnesium Selenocyanate. *Preparation 1.*—Subs. (20°), 0.2648: (1/2) 0.0493 $Mg_2P_2O_7$; (1/2) 0.03037 NH_3.

Preparation 2. Subs. (−33°), 0.5905: (20°) 0.5370; (135°) 0.5033: (2/5) 0.03570 NH_3; (3/5) 0.1221 $Mg_2P_2O_7$.

Calcd. for $Mg(SeCN)_2 \cdot 4NH_3$: Mg, 8.0; NH_3, 22.5. Found (20°): Mg, 8.1, 8.3; NH_3, 22.9, 22.9. Magnesium selenocyanate darkens when heated in a vacuum at 135°, indicating slight decomposition. Approximately six molecules of ammonia are retained by the salt at −33°.

Aluminum Selenocyanate.—Aluminum selenocyanate decomposes slightly when heated in a vacuum at 75°. Subs. (20°), 0.6662, 0.7113, 0.9722; (70°) —, 0.6445; 0.8915: Al_2O_3, (4/5) 0.0657, (3/5) 0.0508, (2/5) 0.0468; Se, No. 3, (1/1) 0.5411. Calcd. for $Al(SeCN)_3 \cdot 5NH_3$: Al, 6.3; Se, 55.5. Found: Al, 6.3, 6.3, 6.4; Se 55.7. Dried in a vacuum at 70°, this salt retained from 2.0 to 2.5 molecules of ammonia.

Zinc Selenocyanate.—This salt melts in a vacuum around 100° with slight decomposition. The zinc cyanide used in Preparation 1 was prepared by the action of an ammonia solution of mercuric cyanide on zinc; that used in Preparation 2 was prepared by adding potassium cyanide to a solution of zinc chloride in water.

Preparation 1. Subs. (20°), 1.1925: (1/5) 0.04764 NH_3; (2/5) 0.2099 $Zn_2P_2O_7$.

Preparation 2. Subs. (20°), 0.8014: (1/1) 0.3721 Se; (2/5) 0.1449 $Zn_2P_2O_7$.

Calcd. for $Zn(SeCN)_2 \cdot 4NH_3$: Zn, 19.0; Se, 46.1; NH_3, 19.8. Found: Zn, 18.9, 19.4; NH_3, 20.0; Se, 46.4.

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[20] Potassium cyanide may be regarded as a potassium ammonocarbonite [Franklin, *J. Phys. Chem.*, 27, 167 (1923)]. Iodine nitridizes potassium cyanide to potassium cyanamide, a potassium ammonocarbonate, for mixed iodocarbonates do not exist.

[21] That is, dried in a vacuum at 20°.

[22] Refers to proportion of substance taken for analysis.

Cupric Selenocyanate.—Copper slowly precipitates mercury from a solution of mercuric cyanide in liquid ammonia with the formation of a mixture of cuprous and cupric cyanides. In contact with an excess of copper, the cupric salt is reduced to cuprous cyanide, which forms colorless crystals moderately soluble in liquid ammonia at room temperatures. Selenium reacts slowly with a solution of this salt to form a strongly-colored blue solution of cupric selenocyanate and a black precipitate of cupric selenide, perhaps in accordance with the equation $2CuCN + 3Se = Cu(SeCN)_2 + CuSe$. The cupric salt was not prepared entirely free from cuprous selenocyanate.

Reactions of Potassium Tetrasulfide, Pentaselenide and Tetratelluride Solutions[22a] with Potassium Cyanide.—The first two salts react with potassium cyanide solution at room temperature to form potassium thio- or selenocyanate and a precipitate, probably of potassium disulfide or diselenide. Potassium tetratelluride and potassium cyanide do not appear to react with each other. It will be remembered that cyanide solutions react with the polysulfide sulfur of ammonium polysulfides to form thiocyanates.

Previous Preparation of Selenocyanates.—Crookes[23] prepared in water solution and analyzed the selenocyanates of potassium, silver, lead and mercury. The selenocyanates of sodium, ammonium, barium, strontium, calcium, magnesium, zinc, iron and copper were prepared but not analyzed. Very little work has subsequently been done on the preparation of selenocyanates.[24]

In conclusion, the author wishes to express his thanks to Dr. C. A. Kraus for his kind and helpful interest in this work.

Summary

1. According to Ruff and Geisel, sulfur dissolves in liquid ammonia in accordance with the reaction $10S + 4NH_3 \rightleftharpoons 6H_2S + N_4S_4$. An entirely analogous reaction takes place when chlorine dissolves in water, $Cl_2 + H_2O \rightleftharpoons HCl + ClOH$. The existence of the first equilibrium has been confirmed by a study of the action of solutions of metallic cyanides upon a solution of sulfur in liquid ammonia. Sulfur dissolves in liquid ammonia in a more complex manner than indicated by the first equation. Preliminary experiments indicate that sulfur solutions contain very appreciable quantities of ammonium polysulfide and sulfur nitride, or the products of the action of sulfur nitride upon an excess of sulfur.

2. Selenium must have an extremely slight solubility in liquid ammonia, such solutions resembling solutions of sulfur in constitution.

[22a] Prepared by the action of a liquid ammonia solution of potassium upon the calculated amounts of sulfur, selenium or tellurium.

[23] Crookes, *Ann.*, **78**, 177 (1851).

[24] Cameron and Davy, *Chem. News*, **44**, 63 (1881). Rosenheim and Pritze, *Z. anorg. Chem.*, **63**, 275 (1909). Muthmann and Schröder, *Ber.*, **33**, 1765 (1900).

3. Sulfur and selenium behave in liquid ammonia as weak nitridizing (oxidizing, de-electronizing) agents.

4. Solutions of cyanides in liquid ammonia react very readily with sulfur and selenium, much more slowly with tellurium, and not at all with arsenic. The following new compounds have been prepared: $Al(SCN)_3 \cdot 5NH_3$, $Mg(SCN)_2 \cdot 4NH_3$, $Mg(SeCN)_2 \cdot 4$ and $6(?)NH_3$, $Zn(SeCN)_2 \cdot 4NH_3$, $Al(SeCN)_3 \cdot 5NH_3$.

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THE CRYSTAL STRUCTURE OF SODIUM PERIODATE

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Introduction

The similarity of crystal form of sodium periodate, $NaIO_4$, and calcium tungstate, $CaWO_4$, as well as of some periodates of other univalent metals and tungstates and molybdates of other bivalent metals, was recognized by Hiortdahl.[1] To these Barker[2] added the compounds $KRuO_4$ and $KOsO_3N$ and discussed the bearing of such cases of isomorphism on valence theory. These crystals are all tetragonal[3] and have axial ratios ranging from 1:1.521 to 1:1.634. Crystallographers have not, however, assigned all of these compounds to the same *class* of symmetry. Thus sodium periodate is given[3] as ditetragonal bipyramidal (D_{4h}), calcium tungstate as tetragonal bipyramidal (C_{4h}), and lead molybdate as tetragonal pyramidal (C_4). The present work casts doubt upon the reality of these differences in symmetry.

From some x-ray-spectrometer measurements it was concluded[4] that in wulfenite, $PbMoO_4$, and scheelite, $CaWO_4$, the metal atoms were placed on two interpenetrating "diamond" arrangements elongated in the direction of the tetragonal axis. These data were theoretically discussed by Niggli and Faesy,[5] and an attempt was made to determine the space-group symmetry; owing, however, to an omission[6] in the space-group tables used, the space group C_{4h}^6 was incorrectly eliminated. In some unpublished work in this Laboratory, Dr. R. M. Bozorth and one of us (R. G. D.) found that symmetrical, basal-plane Laue photographs of wulfenite showed

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[1] Hiortdahl, *Z. Kryst. Min.*, **12**, 411 (1887).

[2] Barker, *J. Chem. Soc.*, **101**, 2487 (1912).

[3] Groth, "Chemische Krystallographie," Engelman, Leipzig, **1908**, vol. 2, pp. 175, 393.

[4] Dickinson, THIS JOURNAL, **42**, 85 (1920).

[5] Niggli and Faesy, *Z. Kryst.*, **59**, 473 (1924).

[6] This omission has since been corrected by K. Weissenberg, *ibid.*, **63**, 173 (1926).

a tetragonal axis and, except for the spots nearest the central image, four symmetry planes;[7] it was further found that, except for this small hemihedry, the intensities of spots occurring on slightly unsymmetrical basal-plane Laue photographs were in accord with the structure factors calculated from the arrangement previously given,[4] completely omitting the oxygen atoms. These facts may be given the following interpretation: (1) the metal atoms have a highly symmetrical arrangement; (2) the slight hemihedry is due to the positions of the oxygen atoms; (3) the hemihedry is noticeable only in the case of simple planes because the reflecting power of the oxygen atoms relative to that of the heavy atoms decreases, as would be expected, with decreasing interplanar distance.

Sodium periodate has been chosen for the present work partly because of its reported higher symmetry, and partly because of the relatively greater weight of the oxygen atoms in it. Moreover, its *structural* similarity to the tungstates and molybdates remained to be demonstrated.

Preparation of the Crystals

Sodium periodate was prepared[8] by passing chlorine into a hot solution of iodine in sodium hydroxide, made by dissolving 20 g. of iodine and 80 g. of sodium hydroxide in 300 cc. of water. After several hours a fine crystal meal separated which, after being filtered and washed, was found to liberate iodine from a slightly basic solution of potassium iodide—a test for periodate.[9] The product was further purified by dissolving it in dil. sulfuric acid and slowly reprecipitating by adding sodium hydroxide. It was then dissolved in water to which a small amount of sulfuric acid had been added, and allowed to crystallize at a temperature of 40° to 45°. The crystals were 3–6 mm. long with the forms $(111)_c$ and $(101)_c$ developed. Throughout this paper the subscript "c" designates those indices which are referred to the crystallographic axes; indices without subscript refer to the space-group axes. The faces were identified by interfacial angle measurements on a reflection goniometer.

A density determination made by displacement of carbon tetrachloride[10] in a pycnometer gave the value 4.12 g./cc. This value is considerably higher than that previously given,[11] 3.865 g./cc. Three analyses were made by adding an excess of potassium iodide to an acid solution of the

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[7] The weakness of the hemihedry of such photographs has also been found by Haga and Jaeger, *Proc. Acad. Sci. Amsterdam*, **18**, II, 1350 (1916), and by Aminoff, *Geol. Fören. Förh.*, **42**, 296 (1920).

[8] See Gmelin-Kraut, "Handbuch der anorganische Chemie," Carl Winter, Heidelberg, **1909**, vol. 1 (2), p. 364.

[9] Treadwell-Hall, "Analytical Chemistry," John Wiley and Sons, New York, **1911**, vol. 2, p. 670.

[10] A. E. H. Tutton, "Crystallography and Practical Crystal Measurement," Macmillan Co., **1911**, pp. 518–534.

[11] Ref. 3, p. 176.

periodate and titrating the free iodine with standard thiosulfate solution. These gave 58.0, 58.4 and 58.7% of iodine; calcd. for $NaIO_4$: 59.3.

Experimental Procedure

Spectral photographs were made by reflecting the K radiation of molybdenum from $(111)_c$, $(110)_c$ and $(001)_c$, using a rotating crystal; to insure precision in the measurements, a reference spectrum of calcite was photographed simultaneously with the spectrum of the periodate. The spectral data are given in Table I.

TABLE I

SPECTRAL DATA FROM SODIUM PERIODATE

hkl	Line[a]	Angle of reflection	$\frac{\lambda}{2 \sin \Theta}$	Order (true unit)	Estimated intensity
(001)	γ	5° 59′	2.978	n_1	0.05
	β	6° 5′	2.977	n_1	.4
	α	6° 49′	2.990	n_1	1.8
	β	12° 10′	1.489	$2n_1$	0.2
	α_1	13° 43′	1.492	$2n_1$	1.0
	α_2	13° 48′	1.493	$2n_1$	0.3
	β	18° 32′	0.993	$3n_1$	.3
$(110)_c$	β	6° 51′	2.644	n_2	.2
	α	7° 39′	2.666	n_2	.9
	β	13° 43′	1.330	$2n_2$	.25
	α_1	15° 25′	1.331	$2n_2$	1.0
	α_2	15° 31′	1.331	$2n_2$	0.6
$(111)_c$	α	4° 12′	4.846	n_3	1
	α	8° 24′	2.432	$2n_3$	0.1
	β	11° 17′	1.612	$3n_3$	.05
	α_1	12° 39′	1.616	$3n_3$	.3
	α_2	12° 44′	1.616	$3n_3$	.1
	γ	14° 51′	1.209	$4n_3$	.05
	β	15° 7′	1.210	$4n_3$	.3
	α_1	17° 1′	1.210	$4n_3$	.8
	α_2	17° 8′	1.209	$4n_3$	.5

[a] The letters refer to the K lines of molybdenum, whose wave lengths are: γ = 0.6197 Å.; β = 0.6311; α_1 = 0.7078; α_2 = 0.7121; when α_1 and α_2 are unresolved they are designated as α and the wave length taken as 0.710 Å.

Laue photographs were taken with the white radiation from a tungsten anticathode; the tube was operated at a peak voltage of 51.5 kv., hence the lower wave-length limit of the x-rays was 0.24 Å. Symmetrical and unsymmetrical photographs were taken through sections ground parallel to $(001)_c$, $(111)_c$ and $(110)_c$. Gnomonic projections of the Laue photographs were made to assist in the assignment of indices to the reflecting planes. Data from these photographs are listed in Table II.

The Unit of Structure

It is convenient first to find the smallest unit of structure compatible with these spectral measurements. From the hemihedry of the Laue photographs, demonstrated below, it follows that the crystal has insufficient symmetry to fix the position of the true H axis as one of two alternatives, but that any possible crystal edge perpendicular to the tetragonal axis must be considered a possible position of the H axis. Let the indices of $(110)_c$ become $(h'k'0)$ when referred to the space-group axes, and those of $(111)_c$ become $(h''k''l'')$. The spectral measurements of Table I lead to the following values: $d_{001} = n_1 \times 2.982$; $d_{h'k'0} = n_2 \times 2.661$; $d_{h''k''l''} = n_3 \times 4.841$; hence $d_{100} = n_2 \sqrt{h'^2 + k'^2} \times 2.661$. Taking 1:1.590 as the axial ratio defining the position of $(111)_c$, it can be shown (for example by considering the intercepts of $(111)_c$ on the original and rotated axes) that $h'':k'':l'' = h'\sqrt{2}\, d_{hk0} : k'\sqrt{2}\, d_{hk0} : d_{001}/1.590\, d_{001} = 3.76\, n_2h' : 3.76\, n_2k' : 1.875 n_1 = 2n_2h' : 2n_2k' : n_1$. If r is the highest integral common divisor of $2n_2h'$, $2n_2k'$ and n_1, then $(h''k''l'') = \left(\frac{2n_2h'}{r}\,\frac{2n_2k'}{r}\,\frac{n_1}{r}\right)$. Substituting these indices and the above values for d_{100} and d_{001}, in the formula: $d_{h''k''l''} = \left[\left(\frac{h''}{d_{100}}\right)^2 + \left(\frac{k''}{d_{100}}\right)^2 + \left(\frac{l''}{d_{001}}\right)^2\right]^{-\frac{1}{2}}$, we get $d_{h''k''l''} = 1.215r$. Since this is equal to $n_3 \times 4.841$, it follows that $r = 4n_3$. We now have only to assign integral values to n_1, n_2, n_3, h and k subject to the restrictions that (1) h and k shall be prime integers, (2) $n_2h'/2n_3$, $n_2k'/2n_3$ and $n_1/4n_3$ shall be prime integers and (3) $n_1n_2^2\,(h'^2 + k'^2)$ shall be as small as possible (since this is proportional to the size of the unit). These conditions are satisfied when and only when $n_1 = 4$, $n_2 = 2$, $n_3 = 1$, $h' = 1$ (or 0), and $k' = 0$ (or 1).

It is thus shown that the smallest possible unit compatible with the spectral data is one having its H and K axes at 45° with the crystallographic axes and having $d_{100} = d_{010} = 5.322$ Å., and $d_{001} = 11.93$ Å. The number of molecules in this unit calculated from our density is 3.94 or evidently 4. When values of $n\lambda$ were calculated for spots occurring on the Laue photographs using this unit and indices referred to it, none was found smaller than 0.26 Å. There is, then, no evidence that the true unit is other than the one described.

The Space Lattice

From the Laue photographs no value of $n\lambda$ was found below 0.48 Å. for any plane having $h + k + l$ odd; thus no such planes gave first-order reflections. This shows that the atomic arrangement is derivable from a space-group based on the body-centered lattice Γ'_t.

The Space Group

A Laue photograph taken with the incident beam nearly perpendicular to (001) showed that spots due to $\{hkl\}$ were not always equal in intensity to those due to $\{khl\}$. The best example of this is shown in Fig. 1, in which the ordinates are estimated intensities and the abscissas $n\lambda$'s. The sharp change in intensity around 0.37 Å. is obviously due to the K absorption edge of iodine. Planes of the form {321} clearly reflect more strongly than those of the form {231}. These data show that there are no planes of symmetry containing the tetragonal axis and that the point-group symmetry is accordingly S_4, C_4 or C_{4h} and *not* D_{4h}.

With the above restrictions as to point group and space lattice, the possible space groups are S_4^2, C_4^5, C_4^6, C_{4h}^5 and C_{4h}^6. In addition to reflections in odd order from planes having $h + k + l$ odd, reflections are required to be absent in the following cases.[12]

S_4^2, C_4^5, C_{4h}^5: none.

C_4^6: reflections from (001) when n is not a multiple of four.

C_{4h}^6: reflections from (001) when n is not a multiple of four; reflections from (hk0) when n is odd.

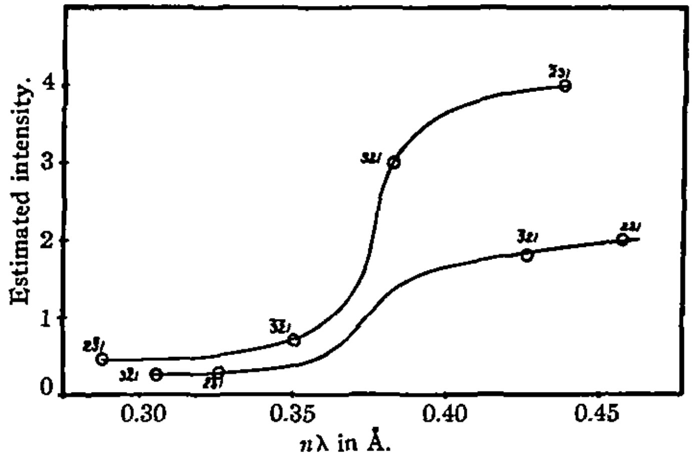

Fig. 1.—Intensities of reflection of {321} {231}.

It has already been shown that for the reflections found from (001) n is a multiple of four. Furthermore, no planes of the type (hk0) were found to reflect in the first order on the Laue photographs although (150), (170), (370) and (350) were in position to do so; and on a transmission spectral photograph where the reflections (110), (330) and (130) had opportunity to appear, these were absent. All of these absences are required by the space group C_{4h}^6, but are not by the others.

The Atomic Arrangement

The coördinates of the general and special positions of C_{4h}^6 are:[13]

Four equivalent positions:

(a) $(0\ \frac{3}{4}\ \frac{1}{8})$ $(0\ \frac{1}{4}\ \frac{7}{8})$ $(\frac{1}{2}\ \frac{1}{4}\ \frac{5}{8})$ $(\frac{1}{2}\ \frac{3}{4}\ \frac{3}{8})$

(b) $(0\ \frac{3}{4}\ \frac{5}{8})$ $(0\ \frac{1}{4}\ \frac{3}{8})$ $(\frac{1}{2}\ \frac{1}{4}\ \frac{1}{8})$ $(\frac{1}{2}\ \frac{3}{4}\ \frac{7}{8})$

[12] Astbury and Yardley, *Phil. Trans.*, 223A, 238 (1924).

[13] Wyckoff, "The Analytical Expression of the Results of the Theory of Space-Groups," *Carnegie Inst. Publ.*, No. 318 (1922).

Eight equivalent positions:

(c) $(0\,0\,0)$ $(\frac{1}{4}\,\frac{1}{4}\,\frac{3}{4})$ $(\frac{1}{2}\,0\,\frac{1}{2})$ $(\frac{1}{4}\,\frac{3}{4}\,\frac{1}{4})$ $(0\,\frac{1}{2}\,0)$ $(\frac{3}{4}\,\frac{3}{4}\,\frac{1}{4})$ $(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})$ $(\frac{3}{4}\,\frac{1}{4}\,\frac{3}{4})$
(d) $(0\,0\,\frac{1}{2})$ $(\frac{1}{4}\,\frac{1}{4}\,\frac{1}{4})$ $(\frac{1}{2}\,0\,0)$ $(\frac{1}{4}\,\frac{3}{4}\,\frac{3}{4})$ $(0\,\frac{1}{2}\,\frac{1}{2})$ $(\frac{3}{4}\,\frac{3}{4}\,\frac{1}{4})$ $(\frac{1}{2}\,\frac{1}{2}\,0)$ $(\frac{3}{4}\,\frac{1}{4}\,\frac{1}{4})$
(e) $(0\,\frac{1}{4}\,u)$ $(\frac{1}{2}, \frac{1}{4}, \frac{3}{4}+u)$ $(\frac{1}{2}, \frac{3}{4}, \frac{1}{2}+u)$ $(0, \frac{3}{4}, \frac{1}{4}+u)$ $(0, \frac{3}{4}, \bar{u})$ $(\frac{1}{2}, \frac{3}{4}, \frac{1}{4}-u)$ $(\frac{1}{2}, \frac{1}{4}, \frac{1}{2}-u)$ $(0, \frac{1}{4}, \frac{3}{4}-u)$

Sixteen equivalent positions:

(f) $(x\,y\,z)$ $(\frac{1}{4}+y, \frac{1}{4}-x, \frac{3}{4}+z)$ $(\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z)$ $(\frac{1}{4}-y, \frac{3}{4}+x, \frac{1}{4}+z)$
$(x, \frac{1}{2}+y, +\bar{z})$ $(\frac{1}{4}+y, \frac{3}{4}-x, \frac{1}{4}-z)$ $(\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z)$ $(\frac{1}{4}-y, \frac{1}{4}+x, \frac{3}{4}-z)$
$(\frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}+z)$ $(\frac{3}{4}+y, \frac{3}{4}-x, \frac{1}{4}+z)$ $(\bar{x}, \frac{1}{2}-y, z)$ $(\frac{3}{4}-y, \frac{1}{4}+x, \frac{3}{4}+z)$
$(\frac{1}{2}+x, y, \frac{1}{2}-z)$ $(\frac{3}{4}+y, \frac{1}{4}-x, \frac{3}{4}-z)$ $(\bar{x}\,\bar{y}\,\bar{z})$ $(\frac{3}{4}-y, \frac{3}{4}+x, \frac{1}{4}-z)$

There is only one distinct way in which the sodium and iodine atoms can be placed, namely Na at (a) and I at (b). In these positions the sodium and iodine atoms contribute nothing to the first-order reflections from the planes (114), (118), (138), (338) and (154), which were found to reflect in the first order; these reflections must be due to the oxygen atoms alone. If the sixteen oxygen atoms are in any combination of the positions (c), (d) and (e) the structure factor for the planes just mentioned remains zero. The only remaining arrangement for the oxygen atoms is (f); the oxygen atoms are thus all in equivalent positions.

A considerable amount of confirmatory evidence is obtainable from the Laue photographs. In order to consider this, it is convenient to divide the first-order reflections into three classes according to their structure factors.

Class 1. h and k both odd; l twice an odd number.
$S = 4\,(\overline{\mathrm{Na}} + \bar{\mathrm{I}})$ + oxygen terms.
Class 2. $h + k$ odd; l odd.
$S = 2\,\sqrt{2}(\overline{\mathrm{Na}} - \bar{\mathrm{I}})$ + oxygen terms.
Class 3. h and k both odd, l twice an even number.
$S = 0$ + oxygen terms.

Neglecting the contribution of the oxygen atoms, the structure factor for Class 1 is much greater than that for Class 2; while that for Class 3 is zero. This is in agreement with the observations; under comparable conditions of $n\lambda$ and interplanar distance, reflections of Class 1 were always found to be stronger than those of Class 2, and those of Class 2 stronger than those of Class 3. Instances of this are shown by the Laue data of Table II. The spectral and Laue data thus lead to the conclusion that sodium periodate has the space-group symmetry C_{4h}^{6} with the sodium atoms at (a), the iodine atoms at (b) and the oxygen atoms at (f).

TABLE II

LAUE PHOTOGRAPHIC DATA FROM SODIUM PERIODATE

INCIDENT BEAM THROUGH (100) = (110).

hkl	Class	d_{hkl}, Å.	$n\lambda$, Å.	Estimated intensity
219	2	1.160	0.42	5
1.1.10	1	1.139	.44	9
$41\bar{5}$	2	1.137	.42	3
$31\bar{8}$	3	1.116	.43	0.05
$0.1.\overline{11}$	2	1.063	.45	2.5
$\bar{2}\ 1.\overline{11}$	2	0.987	.41	2.2
$\bar{5}1\bar{4}$	3	.985	.45	0.02
$\bar{3}.1.\overline{10}$	1	.975	.42	6
$\bar{5}1\bar{6}$	1	.935	.40	5
$\bar{4}1\bar{9}$	2	.934	.39	1.8
$52\bar{9}$	2	.793	.44	0.8
$3.2.\overline{13}$	2	.780	.45	.9
$1.2.\overline{15}$	2	.756	.44	.4
$\bar{1}.2\ 15$	2	.756	.41	.7
$\bar{5}.2.\overline{11}$	2	.732	.45	.3
$\bar{7}21$	2	.730	.45	.7
$\bar{7}23$	2	.720	.44	.3
$\bar{7}2\bar{5}$	2	.701	.42	.5
734	3	.679	.47	.00
$\bar{5}.2.\overline{13}$	2	.672	.39	.2
736	1	.659	.43	.9
$5.3.\overline{14}$	1	.632	.43	.5
$83\bar{1}$	2	.623	.39	.25
$83\bar{3}$	2	.616	.39	.1
$7.3\ \overline{10}$	1	.603	.38	.5
$\bar{8}3\bar{7}$	2	.585	.43	.2
$\bar{8}3\bar{9}$	2	.564	.40	.15

Discussion of the Structure

The arrangement of the sodium and iodine atoms in the unit of structure as well as the general character of the arrangement of the oxygen atoms is shown by the left parallelopiped of Fig. 2. Each iodine atom is surrounded by four equidistant oxygen atoms at the corners of a tetragonal bisphenoid.[14] All of the bisphenoids are alike, but half of them are rotated 90° about a vertical axis from the position of the other half. The bisphenoids may approximate closely to regular tetrahedra but are not required by symmetry to do so. The sodium and iodine atoms form two interpenetrating "diamond" arrangements. This is shown by the right-hand part of Fig. 2, which is a drawing of a unit containing eight molecules of sodium periodate and having its axes parallel to the crystallographic axes; its relation to the

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[14] This remark applies equally well to the sodium atoms; however, on chemical grounds, it is more natural to consider the association of the oxygen atoms to be with the iodine atoms rather than the sodium atoms.

true unit of structure is shown by the numbering of the corresponding sodium atoms.

The sodium and iodine atoms are thus arranged in just the same manner as previously given[4] for the analogous atoms in lead molybdate and calcium tungstate. The fact that sodium periodate, instead of being holohedral, turns out to be tetragonal bipyramidal, strengthens the presumption that the periodates, tungstates and molybdates mentioned in the introduction are structurally even more closely similar than had been supposed.

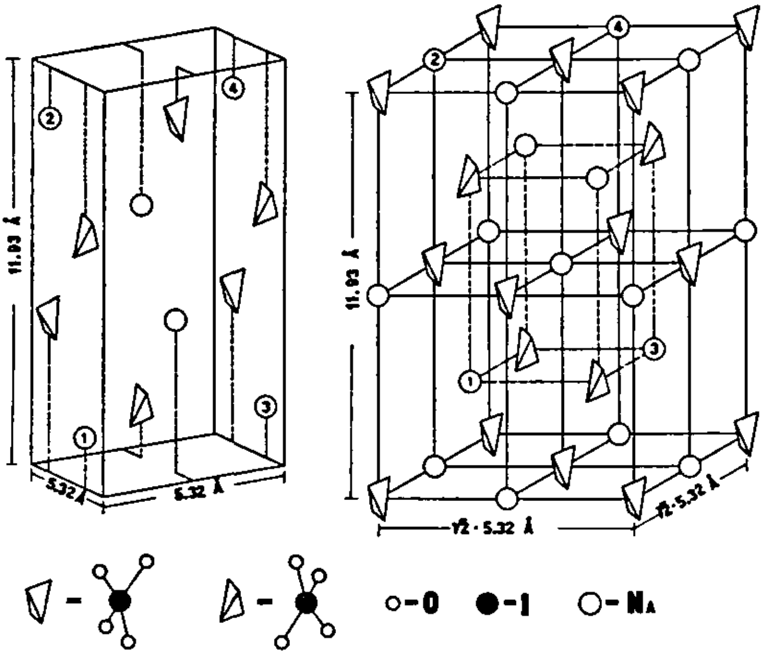

Fig. 2.—Left: the unit of structure of $NaIO_4$. Right: a larger unit which contains 8 $NaIO_4$ and whose axes are the crystallographic axes.

Incidentally, this structure shows that it is unjustifiable to write the formula of solid sodium periodate as $Na_2I_2O_8$, as has sometimes been done.

Summary

The structure of the tetragonal crystal sodium periodate has been investigated using spectral and Laue photographs. The crystal is found not to be holohedral; its space-group symmetry is C_{4h}^6. There are four molecules in a unit having $d_{100} = 5.322$ and $d_{001} = 11.93$ Å. The sodium and iodine atoms are in the no-parameter positions (a) and (b), respectively (see text); the oxygen atoms are all equivalent and in the general three-parameter positions (f).

PASADENA, CALIFORNIA

[Contribution from the Fixed Nitrogen Research Laboratory, United States Department of Agriculture]

THE CHEMICAL ACTION OF GASEOUS IONS PRODUCED BY ALPHA PARTICLES. IX. SATURATED HYDROCARBONS

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Preliminary to a study of its oxidation under the influence of alpha particles, the stability of pure methane was first examined. The absence of change of pressure during exposure to radon mixed with methane in a 2cm. bulb led us to conclude that like carbon dioxide[1] methane is stable under these conditions, and that hence its oxidation probably could be carried out without encountering complications. The latter conclusion was found to be true, but not on account of the assumed stability of methane, the assumption of which now seems to be quite erroneous.[2]

Similar exposure of pure ethane to alpha-radiation gave a more readily apparent result.[3] A liquid phase soon appeared, showing some reaction to be taking place. Similar results were even more readily obtained with propane and with butane. This suggested a reëxamination of the behavior of methane. The residual gases after radiation of methane were separated by fractionation at low temperature, and by using a palladium diffusion apparatus[1] to remove hydrogen. It was found that only about one-fourth of the original methane remained unchanged, despite the constancy of pressure observed. This could readily be accounted for by a reaction such as $2CH_4 = H_2 + C_2H_6$. Further study has shown, however, that other simultaneous reactions must be taken into account in explaining the remarkable constancy of total pressure during the methane reaction. This will be referred to later.

In general, the reactions that all of the paraffins from methane to butane undergo are complicated by simultaneous and successive reactions to such a degree that only their broader aspects have been worked out. On this account we forego attempting to apply the usual equation for velocity of reaction except to the oxidations of methane and of ethane. Some changes of experimental procedure were also necessitated.

Owing to the difficulty of interpreting the manometric data, even with the aid of thermal analysis at low temperatures, it was necessary from time to time to lower the system to liquid-air temperature and to pump off hydrogen and methane for analysis. To provide enough material for this purpose, larger reaction vessels had to be used. This involved the obstacle of not being able to calculate α-ray ionization accurately by the

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[1] Lind and Bardwell, This Journal, **47**, 2690 (1925).

[2] Lind and Bardwell, *Science*, **62**, 422 (1925).

[3] Lind and Bardwell, *ibid.*, **60**, 364 (1924).

average-path method[4] for spheres of such large size. The first expedient was to run two parallel experiments, one in a small sphere for manometry and the calculation of ionization, another in a larger sphere for chemical analysis. This duplication has been rendered unnecessary by a most valuable contribution of Professor W. Mund[5] of the University of Louvain, who has ingeniously solved the problem of calculating ionization produced by radon in spheres, without imposing the former upper limitations as to diameter. We have used Mund's equation successfully, and incidentally can support its validity by having found agreement with values obtained by the average-path method in an intermediate region where both are applicable.

The different saturated hydrocarbons behave similarly in their ionic reactions, as was pointed out in Part VII. Free hydrogen is always eliminated, free carbon never; condensation products result which may be gaseous, liquid or solid, and the reactions continue under further radiation even in the liquid and solid members. Not only is hydrogen liberated but also hydrocarbons lower than the original one are formed. All of this soon gives a mixture of hydrocarbons still interacting; therefore the sample "cuts" should be taken at the shortest intervals feasible in order to maintain conditions as simple and definite as possible.

The experimental methods are in general identical with those previously employed, though the procedure requires some explanation, and a few new methods of analysis and preparation are described in the following sections.

Preparation of Gases.—Methane was taken from the middle fraction of a large supply of liquid methane that Dr. Frank Porter had purified from natural gas from Petrolia, Texas. The boiling points of the first and last thirds of the liquid phase did not differ by more than 0.01°.

Ethane was taken from a large supply prepared by Dr. A. G. Loomis and Mr. J. E. Walters for vapor-pressure measurements. Its purity was demonstrated by the same test as for methane above.

Propane and butane were purified by fractionating commercial grades (about 90%) of these gases, obtained from Dr. A. B. Lamb of Harvard University. The boiling points of the first and last thirds of purified gas did not differ by more than 0.01°. The vapor-pressure tests of purity were made in the cryostat used by Perry and Bardwell[6] and Perry and Porter[7] with platinum-resistance thermometer No. 4.[8]

Methods of Analysis.—The gaseous hydrocarbons separated as products of radiation were tested for unsaturation (see Part VII). They were then exploded with an excess of oxygen and the contraction was measured. The carbon dioxide formed was determined by absorption with potassium hydroxide (see Part VI). This combustion served as an approximate check on the fractionation.

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[4] Lind, "Chemical Effects of Alpha Particles, etc.," Chemical Catalog Co., New York, 1921, p. 82.

[5] Mund, *Ann. Soc. Sci. Brux*, **44**, 336 (1925); *J. Phys. Chem.*, **30**, 890 (1926).

[6] Perry and Bardwell, This Journal, **47**, 2629 (1925).

[7] Perry and Porter, *ibid.*, **48**, 299 (1926).

[8] Loomis and Walters, *ibid.*, **47**, 2851 (1925).

Experimental Procedure.—Experiments on the oxidations of methane and of ethane and preliminary studies of methane, ethane and propane condensations were conducted in small bulbs (2 cm. diameter). The procedure was that described in Part VI. The experiments reported in Tables I, II, III and IV were conducted as follows.

Radon was introduced in the usual manner[1] and measured by its γ-ray activity four hours after the time of introduction. The pure hydrocarbon was then introduced and its pressure measured. After a suitable period of radiation, the total pressure was again measured at room temperature. The bulb was then immersed in liquid air and the hydrogen and methane produced in the reaction were removed by a Toepler pump.[9] The bulb was then brought quickly to room temperature and the total pressure measured. Following another interval of radiation, the total pressure was measured and the hydrogen and methane produced were removed from the bulb in liquid air. This procedure was repeated for several intervals of radiation. The hydrocarbons that are condensable in liquid air were then separated by fractionation using baths at —150°, —125° and —95° for the removal of ethane, propane and butane, respectively, by means of a Toepler pump.

Methane.—Mund and Koch[10] first exposed methane to α-rays. Using 100 millicuries of radon they found a small reduction of pressure amounting to 10 mm. in three days, from which they concluded that a reaction took place which diminished the number of gaseous molecules present. No mechanism of reaction was proposed nor was any observation of liquid droplets recorded.

The results of the present measurements of the condensation of methane under α-radiation of radon are given in Table I. In the column for total pressure, it is shown that the experiment was conducted in stages. At the end of each stage, the reaction sphere was immersed in liquid air boiling at about 4 cm. pressure and all of the hydrogen produced, together with some of the methane, was pumped off and determined separately. After four such operations, all of the methane was pumped off from liquid air. The residue was then allowed to warm, giving gaseous hydrocarbons, ethane, propane, butane and higher homologs and also some liquid, the total quantities of which are shown in the balance sheet of Table I. The gases were subjected to low-temperature rectification; the fractions were analyzed by combustion methods, including the dry thermal absorption of carbon dioxide as described in Part VI.[1] These fractions examined by the copper catalytic method described in Part VII[11] revealed no unsatura-

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[9] In the methane experiment, the liquid air was boiled at about 4 cm. pressure in order to reduce the temperature to about $-200°$, thus diminishing the loss of methane accompanying the removal of hydrogen.

[10] Mund and Koch, *Bull. soc. chim. Belg.*, 34, 120 (1924).

[11] Lind, Bardwell and Perry, This Journal, 48, 1557 (1926).

TABLE I

CONDENSATION OF METHANE

Reaction sphere: vol., 32.00 cc.; diam., 3.940 cm. Temp., 25°. $E_0 = 0.0671$ curie.
Reaction: $2CH_4 \longrightarrow$ (A) $C_2H_6 + H_2$ or (B) $C_2H_4 + 2H_2$.

Time Days	Hours	$e^{-\lambda t}$	P_{total}	Cc. pumped off H_2	Cc. pumped off CH_4	$\frac{M_{H_2}}{N_{\text{total}}}$	$\frac{-M_{CH_4}}{N_{CH_4}}$
0	0	1.00000	730.2				
0	16.17		729.0				
0	20.75	0.85589	Pumped off H_2 and some CH_4	1.01	2.75	1.62	
0	21.5		640.7				
1	20.5		641.2				
1	21.75	.70955	Pumped off H_2 and some CH_4	0.908	0.470	1.66	
1	22.25		609.6				
3	16.33		610.3				
3	17.75	.51013	Pumped off H_2 and some CH_4	1.173	.693	1.63	
3	18.25		567.8				
6	16.00		570.0				
6	17.5	.29685	Pumped off H_2 and some CH_4	1.135	6.580	1.54	
6	18.0		388.5				
6	19		All methane pumped off from liquid air	Total pumped off in previous steps			
6	19.5		Residual pressure 38.1		10.493	1.61	2.2

Analytical Results in Cc. of Gas

	CH_4	H_2	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}
Initial	30.80	...	...	...	...	...
Final	25.24	4.226	0.863	0.296	0.171	0.067

$$\frac{-\Delta CH_4}{\Delta H_2} = \frac{5.56}{4.226} = 1.315$$

Atomic Balance Sheet in Cc.

		C	H
Initial as CH_4		30.80	123.2
Reacted		5.56	22.3
Final in gas phase:			
	as CH_4	25.24	100.96
	C_2H_6	1.726	5.178
	C_3H_8	0.888	2.278
	C_4H_{10}	.684	1.710
	C_5H_{12}	.335	0.804
	H_2		8.452
Total as gases		28.89	119.38
In liquid		1.927	3.84
Emp. formula of liquid $C_nH_{1.98n}$			

Over the whole reaction $\frac{N_{\text{total}}}{N_{CH_4}} = 1.05$

$$\frac{-M_{CH_4}}{N_{CH_4}} = \frac{-\Delta CH_4}{\Delta H_2} \times \frac{M_{H_2}}{N_{\text{total}}} \times \frac{N_{\text{total}}}{N_{CH_4}} = 1.32 \times 1.61 \times 1.05 = 2\ 2$$

There was no hydrogenation of the ethane fraction by the copper catalyst, indicating absence of ethylene or other unsaturated hydrocarbons in the gas phase.

tion in the gas phase either from methane or from any of the other saturated hydrocarbons studied, although the liquid residue at room temperature is always unsaturated according to the empirical formula obtained by difference, which in the case of the residual liquid from methane is $C_nH_{1.98n}$. The speedy removal of unsaturated compounds from the gas phase to the liquid will be discussed in connection with the theory of the condensation itself (see also under "Ethane").

Condensation of Ethane.—Ethane was first examined under α-radiation by Lind and Bardwell[4] and independently by Mund and Koch[5] a little later. Mund and Koch put forward the following theory of reaction in two stages: (1) $C_2H_6 \longrightarrow C_2H_4 + H_2$; followed by (2) $xC_2H_{4g} \longrightarrow (C_2H_4)_x l$. Although they state that Reaction 2 takes place almost immediately, yet they seem to believe that the ethylene molecule formed must first be acted on again by radon before it condenses to liquid, in support of which they described an experiment showing direct condensation of ethylene by α-radiation. The two views hardly seem compatible. If the ethylene formed from ethane must be ionized before it condenses, the rate of reaction will be controlled by the partial pressure of ethylene, its specific ionization, and the ratio $-M_{C_2H_4}/N_{C_2H_4}$ (= 5 as shown in Part VIII).[12] Although the $-M/N$ ratio is considerably greater for ethylene than for ethane, nevertheless the low partial pressure of ethylene formed from ethane would entail a slow rate of disappearance if dependent on its ionization. Our continued failure to find unsaturated hydrocarbons in the gas phase (although they are abundantly indicated in the liquid, and although our theory assumes their momentary existence) forces us to conclude that their condensation is really "immediate," by which we mean that they do not behave like ordinary olefins since they require no further action by α-radiation to condense to liquid. Our theory involves the following reactions by Method A and more rarely by B.

$$C_2H_6 + (\alpha) \longrightarrow C_2H_6^+ + (-);\quad C_2H_6^+ + C_2H_6 \longrightarrow (C_2H_6)_2^+;$$

$$\begin{array}{lll} (A_1) & (C_2H_6)_2^+ + (-) \longrightarrow & \left\{\begin{array}{ll} (1) & C_4H_{10} + H_2 \text{ or} \\ (2) & C_4H_8 + 2H_2 \text{ followed immediately by } xC_4H_{8g} = \\ & (C_4H_8)_x l \end{array}\right. \\ (A_2) & & \end{array}$$

$$(B)\quad (C_2H_6)_2^+ + (-) \longrightarrow CH_4 + C_3H_8$$

From the ratio $-\Delta C_2H_6/\Delta H_2 = 1.31$, A_1 and A_2 appear to occur about in the ratio 1:1. From analysis of the gases evolved $A_{(1 \text{ or } 2)}$ and B occur in the ratio 5:1.

Our mechanism, based on the assumption of a singly charged, 2-molecule cluster preceding elimination of hydrogen, differs from that of Mund and Koch in certain respects. It predicts the higher gaseous hydrocarbons and more of butane than of propane, as found (Table II). The quantity of any one higher hydrocarbon found in the gas phase is, of course, less than would

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[12] Lind and Bardwell, This Journal, 48, 1575 (1926).

be required by the equations just given, because by further ionization it has in part gone to form yet higher gaseous and liquid members. This

TABLE II

CONDENSATION OF ETHANE

Reaction sphere: vol., 32.92 cc.; diam., 3.977 cm. Temp., 25°. $E_0 = 0.0922$ curie.
Reaction: $2C_2H_6 \longrightarrow$ (A) $C_4H_{10} + H_2$ or (B) $C_4H_8 + 2H_2$.

Time				Pumped off				
Days	Hours	$e^{-\lambda t}$	P_{total}	H_2, cc.	CH_4, cc.	H_2, %	$\frac{M_{H_2}}{N_{\text{total}}}$	$\frac{-M_{C_2H_6}}{N_{C_2H_6}}$
0	0	1.00000	1265.8					
0	3.5		1266.0					
0	5.17	0 96199	Pumped off CH_4 and H_2	0.742	0.216	77.5	1.275	
0	5.5		1244.5					
0	22.0		1243.9					
0	23.7	.84051	Pumped off CH_4 and H_2	2.728	.455	85.6	1.35	
0	23.67		1175.0					
1	22.0		1178.5					
1	23.67	.69943	Pumped off CH_4 and H_2	3.474	.763	82.0	1.57	
2	0.17		1086.9					
2	22.33		1089.3					
2	23.5	.58495	Pumped off CH_4 and H_2	2.733	.582	82.5	1.555	
3	0.17		1019.0					1.7

Analytical Results in Cc. of Gas

	C_2H_6	CH_4	H_2	C_3H_8	C_4H_{10}	C_5H_{12}
Initial	54.75	...	....	...	...	...
Final	40.17	2.268	11.156	0.752	1.61	0.125

$$\frac{-\Delta C_2H_6}{\Delta H_2} = \frac{14.58}{11.16} = 1.31$$

Atomic Balance Sheet in Cc.

	C	H
Initial as C_2H_6	109.50	328.5
Reacted	29.16	87.5
Final in gas phase:		
as H_2	.....	22.312
CH_4	2.27	9.072
C_2H_6	80.34	241.02
C_3H_8	2.256	6.016
C_4H_{10}	6.44	16.1
C_5H_{12}	0.625	1.50
Total	91.931	296.020
As liquid	17.57	32.48
Formula $C_nH_{1.85n}$		

Over the whole reaction: $\frac{N_{\text{total}}}{N_{C_2H_6}} = 1.05$

$$\frac{-M_{C_2H_6}}{N_{C_2H_6}} = \frac{-\Delta C_2H_6}{\Delta(CH_4 + H_2)} \times \frac{M_{(CH_4+H_2)}}{N_{\text{total}}} \times \frac{N_{\text{total}}}{N_{C_2H_6}} = 1.085 \times 1.483 \times 1.05 = \mathit{1.69}$$

There was only 0.5% contraction of "ethane cut" in fuming H_2SO_4 as against about 1% shown by pure C_2H_6 under the same conditions. No hydrogenation of "butane cut" could be effected with copper catalyst.

theory takes into account that $-\Delta C_2H_6/+\Delta H_2$ is not equal to 1 (as required by Mund and Koch) but is between 1 and 2 as we find for methane and also for propane and butane, which again fits with the presence of some higher gaseous saturated hydrocarbons.

To explain the immediate condensation of the unsaturated hydrocarbons, we assume that at least two of the four valences left free by the simultaneous removal of $2H_2$ from a 2-molecule cluster, do not immediately satisfy each other and close up, but remain open and act as centers of attraction for other similar open pairs until a large chain or ring compound is condensed out as liquid, thus preventing the accumulation of any unsaturates in the gas phase. The fact that the unsaturated hydrocarbons do not accumulate in the gas phase is not only shown by failure to find them by the catalytic-hydrogenation method, but also by the constancy of gas pressure during reaction, which requires that all three reactions, A_1, A_2 and B, proceed at constant pressure.

Propane and Butane.—Propane and butane (Tables III and IV) behave much like ethane. Both hydrogen and lower hydrocarbons are eliminated, giving the higher members and an increasing amount of liquid (or solid) the higher the initial member.

With propane, if we use a 2cm. sphere and 100 millicuries, the material becomes entirely solid, passing through a vaseline-like stage and finally becoming sufficiently "dry" to draw away from the wall; but when using a sphere of twice the diameter with the same amount of radon, the product is a clear liquid. The difference appears to be due to the amount of radiation received by the liquid phase which determines secondary reaction and consequently whether condensation may lead to appearance of solid. In the small sphere the formation of liquid is completed while there is still sufficient radon to carry the liquid on into the solid state; furthermore, owing to the smaller area, the wall radiation per unit area is four times greater.

General Discussion of the Action of Alpha Particles on Saturated Hydrocarbons

The most striking characteristic of these reactions is the fact that beginning with any pure member of the series, exposure to α-radiation results in the elimination of hydrogen or lower saturated hydrocarbons, thus building up higher members by addition or condensation as a result of valences freed in the process. Soon a mixture of gaseous and later of liquid or eventually of solid phases is present which may contain all members of saturated and unsaturated series up to the highest product attained. To produce by this means sufficient quantities of the liquid or solid phases to permit their separation and identification appears to be a difficult task which has not been attempted in the present work. However, the

TABLE III

CONDENSATION OF PROPANE

Reaction sphere: vol., 34.79 cc.; diam., 4.051 cm. Temp., 25°. $E_0 = 0.0737$ curie.
Reaction $2C_3H_8 \longrightarrow$ (A) $C_6H_{14} + H_2$ or (B) $C_6H_{12} + 2H_2$.

Time				Pumped off				
Days	Hrs	$e^{-\lambda t}$	P_{total}	H_2, cc	CH_4, cc.	H_2, %	$\frac{M_{H_2}}{N_{total}}$	$\frac{-M_{C_3H_8}}{N_{C_3H_8}}$
0	0	1.00000	830.1					
0	17		829.9					
0	19.25	0.86557	Pumped off CH_4 and H_2	2.01	0.423	82.6	1.150	
0	19 5		786.8					
1	19.0		794.1					
1	19.5	.72163	Pumped off CH_4 and H_2	2.16	.724	74.8	1.30	
1	19.75		734.5					
2	17.75		740.3					
2	18 5	.60730	Pumped off CH_4 and H_2	1.78	.554	76.2	1.365	
2	19 0		690.8					
4	17.5		703.4					
4	18.75	.42292	Pumped off CH_4 and H_2	2.685	.655	80.3	1.27	
4	19 0		632.5				Wtd.	
7	17.0		643.9				Av. 1.263	
7	18.0		Pumped off from liq. air	2.37	.665	78.1		
7	18.25		576.8	11.005	3.021			1.74

Analytical Results in Cc. of Gas

	C_3H_8	CH_4	H_2	C_2H_6	C_4H_{10}	C_5H_{12}
Initial	38.0	...	....	...	...	..
Final	20.93	3.021	11.005	1.763	2.120	1.59

$$\frac{-\Delta C_3H_8}{\Delta(H_2)} = \frac{17.07}{11.01} = 1.54$$

Atomic Balance Sheet in Cc.

	C	H
Initial as C_3H_8	114.00	304.00
Reacted	51.2	136.6
Final as gases:		
as H_2	.....	22.01
CH_4	3 021	12.084
C_2H_6	3 526	10.578
C_3H_8	62.79	167.44
C_4H_{10}	8.48	21.20
C_5H_{12}	7 95	19.08
Total	85.76	252.39
As liquid	28.23	51.61
Formula of liq. $C_nH_{1.83n}$		

$$\text{Over the whole reaction: } \frac{N_{total}}{N_{C_3H_8}} = 1.137$$

$$\frac{-M_{C_3H_8}}{N_{C_3H_8}} = \frac{\Delta C_3H_8}{\Delta(CH_4 + H_2)} \times \frac{M_{(CH_4+H_2)}}{N_{total}} \times \frac{N_{total}}{N_{C_3H_8}} = 1.216 \times 1.263 \times 1.137 = \mathit{1.74}$$

No hydrogenation of the butane cut could be effected with copper catalyst.

TABLE IV

CONDENSATION OF BUTANE

Reaction sphere: vol., 33.21 cc.; diam., 3.988 cm. Temp., 25°. $E_0 = 0.1216$ curie
Reaction: $2C_4H_{10} \longrightarrow$ (A) $C_8H_{18} + H_2$ or (B) $C_8H_{16} + 2H_2$.

Time				Pumped off				
Days	Hrs.	$e^{-\lambda t}$	P_{total}	H_2, cc.	CH_4, cc.	H_2, %	$\frac{M_{H_2}}{N_{\text{total}}}$	$\frac{-M_{C_4H_{10}}}{N_{C_4H_{10}}}$
0	0	1.00000	825.5					
0	21.5		830.5					
0	22.0	0.84789	Pumped off CH_4 and H_2	4.391	0.769	85	1.163	
0	22.25		717.1					
1	16.75		724.7					
1	17.75	.73253	Pumped off CH_4 and H_2	3.160	.550	85.1	1.195	
1	18		642.1					
2	17.25		656.4					
2	17.75	.61187	Pumped off CH_4 and H_2	2.955	.565	84	1.21	
2	18.0		576.6					
3	17.0		591.2					
3	17.5	.51109	Pumped off CH_4 and H_2	2.301	.439	84	1.245	
3	18.0		528.8					
6	16.75		557.3					
6	17.5	.29685	Pumped off CH_4 and H_2	4 268	.812	84	1.263	
6	17.75		441.0	17.075	3.135	Wtd.		
						Av.	1.21	1.8

Analytical Results in Cc. of Gas

	C_4H_{10}	CH_4	H_2	C_2H_6	C_3H_8	C_5H_{12} and higher
Initial	36.10	...	....	..	..	...
Final	11.41	3.135	17.075	3.42	2.83	1.615

$$\frac{-\Delta C_4H_{10}}{\Delta H_2} = 1.44$$

Atomic Balance Sheet in Cc.

	C	H
Initial as C_4H_{10}	144.4	361.0
Reacted	98.8	246.9
Final as gases:		
as H_2	.....	34.150
CH_4	3.135	12.440
C_2H_6	6.84	20.52
C_3H_8	8.49	22.64
C_4H_{10}	45.64	114.10
C_5H_{12}	8.075	18.38
Total	72.180	222.23
As liquid	72.22	138.77
Formula of liq. $C_nH_{1.9n}$		

Over the whole reaction: $\frac{N_{\text{total}}}{N_{C_4H_{10}}} = 1.205$

$$\frac{-M_{C_4H_{10}}}{N_{C_4H_{10}}} = \frac{-\Delta C_4H_{10}}{\Delta(CH_4 + H_2)} \times \frac{M_{(CH_4+H_2)}}{N_{\text{total}}} \times \frac{N_{\text{total}}}{N_{C_4H_{10}}} = 1.222 \times 1.21 \times 1.205 = 1.78$$

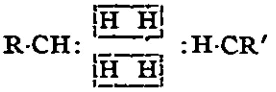
No hydrogenation of the C_3H_8 cut could be effected with copper catalyst at 170°.

residual and in most cases the intermediate fractions of *gas* have been carefully analyzed and support the statements just made. The absence of unsaturated hydrocarbons in the gas phase has been discussed. The empirical formula of the liquid phase indicates unsaturation in all cases.

Geologically it is interesting that this furnishes a method by which the higher hydrocarbons may be built from the lower in nature. The α-radiation in the earth's crust is of very low intensity, yet continued over long geological periods it produces large total effects. *The almost complete absence of hydrogen in most natural gases*, while well recognized, is difficult to explain on this basis unless it be removed by some selective action like the reduction of metallic oxides, which action may also be enhanced by contact catalysis.

The constancy of the ratio in which hydrogen and methane are eliminated from the different members above methane is notable. The following general methods of linkage are suggested.

(1) $R\cdot CH_2.\ \boxed{H\ \ H}\ .H_2\ C\cdot R'$

(2) 

$R\cdot CH:\ \begin{array}{c}\boxed{H\ \ H}\\ \hline \boxed{H\ \ H}\end{array}\ :H\cdot CR'$

(3) $R\cdot\boxed{CH_3\ \ H}\ .H_2\ C\cdot R'$

(4) $R\cdot\boxed{CH_3\ \ CH_3}\cdot R'$

Just why the ratio should be nearly $5H_2:1CH_4$ is not evident. Methane may result from the removal of one of the electrons constituting the carbon-to-carbon bond. On a simple basis of numerical probability the ratio would be $3H_2:1CH_4$ but it is quite conceivable that other considerations, possibly steric ones, may cause the rupture to occur in the ratio $5H_2:1CH_4$.

The assumption that we make of a 2-molecule cluster being formed before reaction takes place is supported by the M/N ratio of 2, and is in agreement with the same kind of indirect evidence from many other reactions.[13] The further assumption, however, that the 2-molecule cluster is formed on the *positive* ion is based on the evidence that free electrons have little affinity for hydrocarbon molecules.[14]

Summary of Results for Hydrocarbons

Table V contains a summary of results, some of which deserve special attention.

The second column, $-M_{\text{H.C.}}/N_{\text{H.C.}}$[15] designates the number of molecules of original hydrocarbon (of the kind indicated by Col. 1) reacting per ion pair produced on that hydrocarbon. The value 2 conforms with our general theory as already explained, and is seen to be independent of the nature of the hydrocarbon and of all other variables.

Col. 3, $-\Delta\text{H.C.}/\Delta H_2$, shows the ratio of disappearance of H.C. mole-

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[13] Lind, *Science*, 64, 1 (1926).

[14] Loeb, *Phil. Mag.*, [6] 43, 229 (1922).

[15] In the following, "H. C." is used as a general abbreviation for hydrocarbon.

TABLE V

CONDENSATION OF SATURATED HYDROCARBONS BY α-RADIATION. SUMMARY OF RESULTS FOR CH_4, C_2H_6, C_3H_8 AND C_4H_{10}

Initial H C.	$\frac{-M_{H\ C}}{N_{H\ C}}$	$\frac{-\Delta_{H\ C}}{\Delta_{H_2}}$	$\frac{\Delta_{H_2}}{\Delta(H_2 + CH_4)}$	H C. reacted, %	In liquid phase Atoms reacting, % C	H	Formula
CH_4	2.2	1.32	..	18.1	34 7	17 2	$C_nH_{1.98n}$
C_2H_6	1.7	1.31	0 83	26.7	60.0	37.2	$C_nH_{1.86n}$
C_3H_8	1.7	1.54	.79	44.8	55.0	37 8	$C_nH_{1\ 83n}$
C_4H_{10}	1.8	1.44	.84	68.4	73.2	56 2	$C_nH_{1.90n}$
			Av. .82				

Initial H C.	In gas phase (% of total C atoms reacted) CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12} or higher	Found	% H free, calcd. for H_2	$(5H_2 + 1CH_4)$
CH_4	...	31.0	16.0	12.3	6.0	37.8	37.5	..
C_2H_6	7.8	...	7.8	22.1	2.2	25 5	25.0	20.8
C_3H_8	5.9	6.9	...	16.6	15.5	16.1	18.75	15.6
C_4H_{10}	3.1	6.9	8.6	..	8.1	13.9	15 00	12.5

cules per hydrogen molecules generated. A value *1.33* corresponds to a 50:50 split of two double clusters, 2(H.C.)$_2$, one breaking to eliminate one and the other, two hydrogen molecules per cluster, thus giving three molecules of hydrogen from four molecules of the hydrocarbon. Propane and butane depart slightly in the direction of too little hydrogen or less unsaturation of products. This will be more clearly brought out below.

Col. 4, $\Delta H_2/\Delta(H_2 + CH_4)$, shows the portion of hydrogen in the hydrogen and methane mixture liberated from the hydrocarbons above methane. The ratio is approximately 5:1 and fairly constant for the different members. Elimination of methane to provide linkage seems to be required theoretically to obtain odd members from even, because mere doubling or cross reactions could not produce any odd members. Ethane is probably produced by direct elimination, according to Method 4 above but is also the result of the condensation of secondary methane.

Col. 5 showing the per cent. of reaction is, of course, dependent on many circumstances capable of arbitrary control and of no fundamental importance, but it will be observed how much more reaction is obtained with the higher members, other things being equal. This is due to their superior stopping power giving more ionization, not to any greater efficiency of the ionization once produced (see Col. 2).

The columns for liquid phase show the greater tendency for the higher hydrocarbons to give liquid upon reacting. The percentage of liquid referred to the original gases would show a yet greater percentage of condensation by the heavy members, for the three reasons that they have not far to go to become liquid, they absorb more energy to promote the process, and produce more liquid in condensing from the same gas volume.

Among the gas-phase data, those for free hydrogen appear to have especial theoretical significance. Taking them in order, for methane we should predict for the primary liberation of hydrogen, 37.5% of the total hydrogen in the methane reacting, according to the following:

			Free hydrogen, %	
			Calcd.	Found
For Methane:	50% A:	$2CH_4 = C_2H_6 + H_2$		
	50% B:	$2CH_4 = C_2H_4 + 2H_2$		
		16H 6H =	37.5	37.8
For Ethane:	50% A:	$2C_2H_6 = C_4H_{10} + H_2$		
	50% B:	$2C_2H_6 = C_4H_8 + 2H_2$		
		24H 6H =	25	25.5
		or taking account of CH_4 also[16]	20.8	
			Free hydrogen, %	
			Calcd.	Found
For Propane:	50% A:	$2C_3H_8 = C_6H_{14} + H_2$		
	50% B:	$2C_3H_8 = C_6H_{12} + 2H_2$		
		32H 6H	18.75	16.1
		or taking account of CH_4	15.6	
For Butane:	50% A:	$2C_4H_{10} = C_8H_{18} + H_2$		
	50% B:	$2C_4H_{10} = C_8H_{16} + 2H_2$		
		40H 6H =	15	13.9
		or taking account of CH_4	12.5	

This appears to furnish a striking confirmation of the special condensation theory assuming an equal chance of the formation of saturated and of unsaturated hydrocarbons. In fact, the agreement appears too good since no account has been taken of hydrogen generation nor of hydrocarbon loss through secondary reaction of products and of liquid; also some of the lower hydrocarbons like methane or ethane would be regenerated by elimination from higher products. Evidently these various secondary processes would be in part compensatory. The fact that agreement with the theory of the primary reaction is so good indicates the compensations to be fairly exact.

Although not giving the better direct agreement, the comparison which includes elimination of methane with that of hydrogen as a means of linking two hydrocarbons is the one apparently more closely related to the facts, and also the more logical in that the amount of free hydrogen found is greater than that calculated, thus leaving a margin to account for some additional hydrogen generation by secondary reaction.

The entire ensemble of series and parallel reactions is too complicated to analyze completely, but some of the most prominent characteristics may be mentioned and others can probably be developed by further study of the data. Methane forms less liquid than predicted directly from the unsaturated hypothesis, while ethane, propane and butane all form somewhat more. The latter is to be expected from formation of saturated liquid

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[16] This is done by assuming that for each six linkages five will be provided by eliminating hydrogen and one by the methane route; we therefore deduct $^1/_6$ of the theoretical hydrogen before comparison with that found.

members by further direct doubling with elimination of hydrogen. In the case of methane, on account of the determination of liquid by a difference method, the small amount reported is subject to larger error. When ethane is radiated the quantity of butane formed exceeds all members with an odd number of carbon atoms in the molecule, thus supporting the direct-doubling theory.

Reactions of Oxidation

Methane.—It has been stated already that a study of the oxidation of methane was undertaken on the assumption that methane itself was stable under α-radiation. It was found that the reaction with oxygen proceeds regularly according to the equation $CH_4 + 2O_2 = CO_2 + 2H_2O$. The assumed clusters from one ion pair are $(O_2{\cdot}CH_4{\cdot}O_2)^+ + (O_2^-{\cdot}CH_4{\cdot}O_2) = 2CO_2 + 4H_2O$. Experimentally we find *1.5* CO_2 + *3.0* H_2O per ion pair. The oxidation is exclusive; no hydrogen is found at the end of the reaction, nor does the kinetics indicate any, since the reaction proceeds at all stages proportionally to the radon present and to the pressure of the reactants. The results are shown in Table VI. The deficiency of carbon dioxide at the end of the reaction is probably due to its having reacted to some extent with methane, which will be discussed later.

Table VI

Oxidation of Methane

Reaction sphere: vol., 4.005 cc.; diam., 1.971 cm. Temp., 25°. $E_0 = 0.1026$ curie.
Reaction: $CH_4 + 2O_2 = CO_2 + (2H_2O)$. Mixture, $1CH_4{:}2O_2$.
Spec. ionization of mixt. 1.09

Time		Radon		Pressure, mm $CH_4 + 2O_2$, calcd.	CO_2, calcd.	Velocity constant $(k\mu/\lambda)'$	$-\frac{M_{(CH_4+O_2)}}{N_{(CH_4+O_2)}}$
Days	Hrs	$e^{-\lambda t}$	Total				
0	0	1.00000	690.2	665.5	24.7	..	...
0	3	0.97775	652.4	608.8	43.6	38.9	4.4
0	6	.95600	619.5	559.5	60.0	38.0	4.3
0	9.5	.93123	586.6	510.1	76.5	36.3	4.1
0	19.5	.86395	507.2	391.0	116.2	38.5	4.4
1	2.0	.82283	469.7	334.8	134.9	36.9	4.2
1	9.0	.78075	434.5	282.0	152.5	39.8	4.5
1	19.5	.72163	394.7	222.3	172.4	39.2	4.4
2	8.5	.65460	358.8	168.4	190.4	40.3	4.6
2	20.0	.60050	336.2	134.5	201.7	40 5	4.6
3	20.0	.50161	308.0	92.2	215 8	37.2	4.2
4	21.0	.41582	290.9	66.5	224.3	37.0	4.2
5	20.0	.34994	281.5	52.5	229.0	35.2	4.0
7	6.5	.27018	273.0	39.7	233.3	34.0	3.8
8	20.0	.20393	268.4	32.8	235.6	(28.2)	(3.1)
17	3.5	.04570	254.8	12.4	242.4	(59.9)	(6.7)
29	13.7	.00488	251.3	7.2	244.1	(131.5)	(14.7)
					Wtd. av.	37.8	4.3
				O_2 22.2			
Analysis			252.0	CH_4 13.7	216.1		

Experiments were made also with excess of oxygen and with excess of methane which gave values of $-M/N$ between 4.2 and 5.1, or practically the same as for stoichiometric mixture, thus showing that the ions of both methane and of oxygen are effective and about equally so.

The values of $-M/N$ are lower than that calculated, 6, but the latter is attained in the presence of 1 molar % of selenium diethyl, as will be shown in a later paper.

The theory of the exclusivity of oxidation is the same as that set forth for the oxidation of carbon monoxide.[1]

Oxidation of Ethane.—The results for the oxidation of ethane are entirely similar to those for methane except for a drop in velocity constant which sets in when the reaction is about 50% complete. Oxidation is complete to water and carbon dioxide; no liquid phase except water appears. Results are shown in Table VII. The assumed clustering and resulting reaction are $(O_2{\cdot}O_2{\cdot}C_2H_6{\cdot}O_2{\cdot}O_2)^+ + (O_2{\cdot}C_2H_6{\cdot}O_2{\cdot}{}^-O_2) = 4CO_2 + 6H_2O$; found per each ion pair: $3CO_2 + 4.5H_2O$.

TABLE VII

OXIDATION OF ETHANE

Reaction sphere: vol., 4.095 cc.; diam., 1.985 cm. diam., 25°. E_0, 0.1551 curie. Reaction: $2C_2H_6 + 7O_2 = 4CO_2 + (6H_2O)$. Mixture, $2C_2H_6{:}7O_2$. Spec. ionization of mixt., 1.286.

Time		Radon		Pressure, mm.		Velocity	
Days	Hrs.	$e^{-\lambda t}$	Total	$C_2H_6 + O_2$, calcd.	CO_2, calcd.	constant $(k\mu/\lambda)'$	$\frac{-M_{(C_2H_6+O_2)}}{N_{(C_2H_6+O_2)}}$
0	0	1.00000	702.6	702.6	0	..	...
0	1.5	0.98882	658.9	623.9	35.0	68.5	6.7
0	3.0	.97775	620.3	554.5	65.8	68.4	6.7
0	4.5	.96682	589.0	498.1	90.9	63.3	6.2
0	8.5	.93824	526.6	385.8	140.8	57.6	5.7
0	10.5	.92428	502.6	342.6	160.0	54.9	5.4
0	21.0	.85428	424.4	201.8	222.6	48.8	4.8
1	3.5	.81363	408.1	172.5	235.6	24.9	2.4
2	1.0	.69246	364.9	94.7	270.2	32.0	3.1
2	21.0	.59603	342.8	55.0	287.8	36.3	3.5
4	2.5	.47773	329.4	30.8	298.6	31.6	3.1
8	2.5	.23256	319.4	12.8	306.6	23.4	2.3
∞	...	.00000	318.1	10.5	307.6	5.5	0.5
Final analysis			315.0	4.0	311.0		

Comparison.—Both for methane and ethane the efficiency of the oxidation reaction is only about 75% of the stoichiometric theory, which requires 6 and 9, respectively, of total molecules reacting per ion pair. Comparison of the $(k\mu/\lambda)'$ values near the beginning of the two reactions shows that the "clean up" of ethane and oxygen is proceeding nearly twice as fast as in the case of methane. Since the specific ionizations of the mixtures are 1.286 and 1.08, respectively, it is evident that the greater rate for ethane is due more to its higher clustering power than to the specific ionization of the mixture, which is greater by only 18%. The velocity of ethane oxidation drops sharply when the reaction is about 70% complete. It is possible that toward the end of the experiment, oxidation is not complete in a single stage (see oxidation of propane and butane below).

Propane and Butane.—The oxidations of propane and of butane do not follow the course of those of methane and ethane. Oxidation is not complete; liquid products other than water appear, indicating partial oxidation. The oxidation of propane can be pushed to completion by prolonged radiation, but the general kinetic equation does not apply and apparently complete oxidation has taken place in successive steps, as contrasted with those of methane and of ethane.

Reaction of Methane with Carbon Dioxide.—In an experiment with excess of methane over oxygen, it was observed that the pressure diminution did not cease upon exhaustion of all the oxygen, but proceeded at a steady, though slower, rate. Since it has already been shown that neither methane nor carbon dioxide alone produces change of pressure, it appeared that the excess of methane must be reacting with the carbon dioxide formed in the reaction, to cause a further lowering of pressure. A new experiment starting with $1CH_4{:}1CO_2$ confirmed this supposition. Liquid droplets that did not appear to be water deposited in regular distribution on the wall and later a wax-like solid appeared. Thénard and Berthelot[17] obtained a similar product on subjecting a mixture of methane and carbon dioxide to the action of a silent discharge ("effluve"). The fact that the partial pressure of the gas, permanent at —150°, diminished at the same rate as that of the condensable gas led us to believe that a direct 1:1 addition product of methane and carbon dioxide was being formed which would be a polymer of formaldehyde. Final analysis, however, showed that the methane had been largely replaced by hydrogen as permanent gas. The entire reaction does not appear, however, to be one between secondary hydrogen and carbon dioxide[1] since this would require an induction period, which does not occur. The ratio $-M_{\text{total}}/N_{\text{total}} = 0.76$ is too low to assume that each positive ion, CH_4^+ or CO_2^+, can add to carbon dioxide or methane, respectively, which would require $-M/N = 2$. There is also no reason to expect any exclusivity of reaction, so that both carbon dioxide and methane can either combine each with the other or undergo their separate actions, depending on whether their positive ions react with their own

Probability	Cluster reaction	Change of press.	$-M_{\text{total}}/N_{\text{total}}$
0.3	$CO_2^+ + CO_2 \longrightarrow 2CO_2$	None	0
.3	$CO_2^+ + CH_4 \longrightarrow (H.CHO)_x$Solid	−2 vols.	2
.2	$CH_4^+ + CO_2 \longrightarrow (H.CHO)_x$Solid	−2 vols.	2
.2	$CH_4^+ + CH_4 \longrightarrow C_2H_6 + H_2$	None	0
	or $(C_2H_4)_x + 2H_2$	None	0

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[17] Berthelot, "Essai de Mécanique Chimique," Dunod, Paris, 1879, vol. 2, p. 383.

molecules or with the opposite kind. We therefore conclude that the complete reaction may be analyzed into the preceding simultaneous reactions, in which the electron, as in many other similar cases, has no function other than the final neutralization of the cluster.

The net result would be $-M/N_{(\text{total})} = 1$ (compare 0.76 found).

Toward the end of the reaction most of the pressure change is doubtless due to interaction of hydrogen and carbon dioxide.

It is a pleasure to acknowledge the assistance of Dr. A. G. Loomis, Mr. J. E. Walters and Dr. Frank Porter of the Cryogenic Laboratory of the United States Bureau of Mines in furnishing us with pure ethane and methane and in giving us valuable advice concerning the fractionation of propane and of butane, and of Professor A. B. Lamb of Harvard University in kindly giving us commercial grades of the two latter gases.

Summary

Under the action of α-radiation from radon in a gaseous mixture, the following reactions have been observed with saturated hydrocarbons.

1. Ethane, propane or butane each condenses with the elimination of hydrogen and methane (approximately $5H_2:1CH_4$) to give higher hydrocarbons, gaseous, liquid or solid, saturated and unsaturated. Methane eliminates hydrogen only.

2. The higher the initial hydrocarbon, the more readily the liquid or solid (if the liquid be sufficiently radiated) phase will be attained.

3. Analysis of the gaseous products shows the presence of all saturated members either higher or lower than the original one. Unsaturated compounds are absent in the gaseous state, which indicates immediate condensation of a freshly formed (nascent) unsaturated hydrocarbon to form liquid; a theory is proposed for this behavior. The resulting liquids contain a large proportion of unsaturated hydrocarbons.

4. The ratio $-M_{\text{H.C.}}/N_{(\text{ions})} = 2$ is interpreted as the clustering of two hydrocarbon molecules per each ion pair. The permanent bond is established by eliminating hydrogen, or 2 hydrogens (formation of unsaturated hydrocarbon) or of methane and probably in other ways.

5. The ratio, $-\Delta_{\text{H.C.}}/\Delta H_2$ = about 1.33, indicates a fairly even division between formation of saturated and unsaturated hydrocarbons.

6. Complete oxidation of methane or ethane by oxygen takes place in one step, indicating the following ion cluster reactions per ion pair:

$$(O_2\cdot CH_4\cdot O_2)^+ + (O_2^-\cdot CH_4\cdot O_2) = 2CO_2 + 4H_2O$$

and $$(O_2\cdot O_2\cdot C_2H_6\cdot O_2\cdot O_2)^+ + (O_2^-\cdot C_2H_6\cdot O_2\cdot O_2) = 4CO_2 + 6H_2O$$

Experimental values for methane were $1.5CO_2$ and $3H_2O$; for ethane, $3CO_2$ and $4.5H_2O$ per ion pair, or 75% of that calculated in each case.

7. The oxidation of propane and butane is not complete in one step. Liquid partial-oxidation products appear.

8. Addition of methane and carbon dioxide was shown. A caramel- or wax-like solid was deposited on the wall.

9. In the oxidation of methane by oxygen, mixtures with excess of either component gave approximately the same —M/N ratio as the stoichiometric mixture, showing the ions of both components to be equally effective in the chemical reaction.

WASHINGTON, D. C.

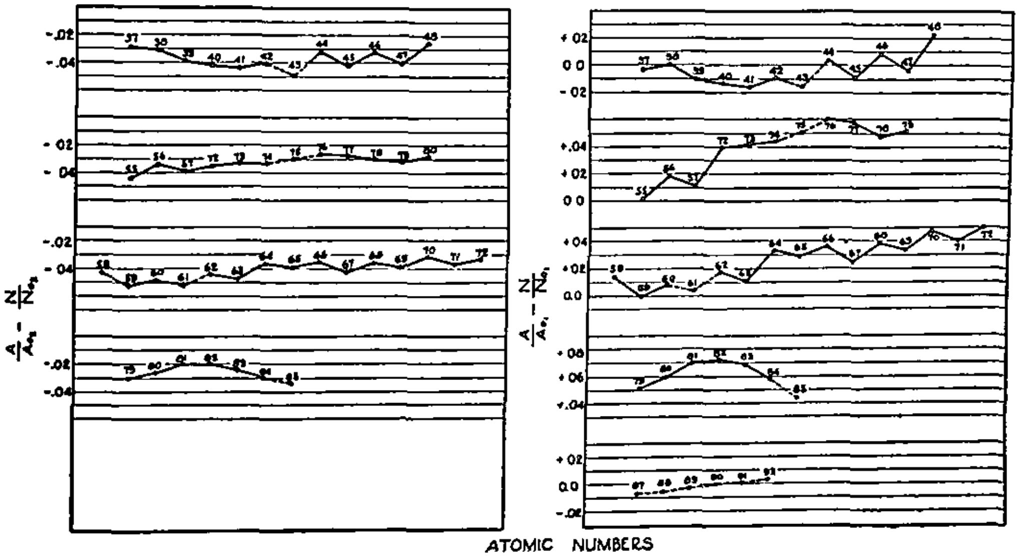
[CONTRIBUTION FROM THE BUREAU OF STANDARDS, UNITED STATES DEPARTMENT OF COMMERCE]

A METHOD OF ESTIMATING ATOMIC WEIGHTS WITH THE AID OF THE PERIODIC LAW

BY EDWARD W. WASHBURN[1]

RECEIVED JULY 23, 1926 PUBLISHED SEPTEMBER 4, 1926

A relationship between atomic weight and atomic number proposed by Harkins and Wilson[2] holds with a fair degree of accuracy for most of the elements in the first three rows of the periodic chart. For the elements beyond nickel, however, the relation fails, probably in part at least because many of these elements are mixtures of several isotopes. All of the elements whose atomic weights have not yet been determined fall in the last five rows of the periodic chart.



The following graphical method, when applied to these elements, exhibits a relation between atomic weight and atomic number which can apparently be applied with considerable confidence to the estimation of most of the missing atomic weights. The method is as follows.

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[1] Chief of the Chemistry Division of the United States Bureau of Standards.

[2] Harkins and Wilson, THIS JOURNAL, 37, 1386 (1915).

The ratio of the atomic weight of each element to that of the next preceding (also succeeding) zero-group element is computed. The ratio of the corresponding atomic numbers is also obtained and the difference between these two ratios is plotted against the atomic numbers of the elements. These graphs for Rows 1, 2, 3, 4 and 6 of the periodic chart are rather irregular and could not be used with much confidence for the prediction of atomic weights. Fortunately, there are no unknown atomic weights for the elements in these rows of the chart. For the remaining rows of the chart the graphs exhibit a considerable degree of regularity and the differences between the two ratios A_x/A_0 and N_x/N_0 become smaller as the atomic numbers increase. Indeed, for the last row in the chart this difference is close to zero. These graphs are shown in the accompanying figure. The estimated loci of the points for the elements whose atomic weights have not been experimentally determined are shown on the dotted portions of the graphs. From these estimated points it is obvious that the missing atomic weights can be computed by reversing the calculation. The "best" values thus estimated are given in Table I.

TABLE I

ESTIMATED ATOMIC WEIGHTS

Symbol	Name	At. no.	At. wt., estimated
Ma	Masurium	43	97.5? (or 98.8)
Il	Illinium	61	146.0
Re	Rhenium	75	187.4
	Eka-iodine	85	212
	Eka-cesium	87	223
Ac	Actinium	89	229
Pa	Proto-actinium	91	234

WASHINGTON, D. C.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 9]

ABSORPTION COLORS OF THE SECOND ORDER

BY JEAN PICCARD

RECEIVED MAY 13, 1926 PUBLISHED SEPTEMBER 4, 1926

Some years ago Piccard and Kharasch isolated *p*-nitrosotriphenylamine and explained its orange color as a color of the second order. We may here briefly review the theory of absorption colors of the second order. As a rule, any increase of the molecular weight of a colored organic compound shifts its color in a definite direction, that is, from yellow to orange to red to violet to blue, and finally to green. If we increase the molecular weight still more, this green color turns to yellowish-green and then to yellow. As this phenomenon reminds us of the interference colors of the

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[1] Piccard and Kharasch, THIS JOURNAL, 40, 1074 (1918).

second order we gave these new colors the name of absorption colors of the second order.[2] This regular development of colors does not stop at the yellow, but we were able to proceed until an orange of the second order had been obtained and we have now reached a red, which is even tinged with violet. During these investigations my collaborators and I were obliged to prepare many new organic bases of very high molecular weight, the last one being tetrabiphenylbenzidine, $C_{60}H_{44}N_2$. These compounds will be described in a following paper.

It was, of course, desirable to find a theory for the formation of the colors of the second order. The following explanation is obvious: the color of ordinary yellow dyes is produced by an absorption band or a group of bands, entering the spectrum from the violet end. When the violet light is absorbed we observe its complementary color, yellow; when the absorption band goes into the blue, we see orange and so on until the band has reached the red end of the spectrum and the dye becomes green. If by further increase of the weight we produce a further shifting of the band, it will leave the visible part of the spectrum. Experience shows that in this case we do not obtain a colorless compound, but that a new band, which is the "octave" of the first one, always enters the visible part of the spectrum at its violet end and we then get the yellow of the second order.

To prove the correctness of this theory we had to show first that the described phenomenon is not merely accidental. For this purpose we prepared numerous dyes showing colors of the second order and there is now no doubt that from an empirical point of view our theory has been successful. From a theoretical point of view, however, it was very desirable to prove that the absorption band which we had seen disappearing at the red end of the spectrum has really entered the infra-red.

The observation of the infra-red spectrum is a rather difficult task and I am grateful to Professor Victor Henri at the University of Zürich for helping me with much advice, as well as for allowing me to work as a guest in his Laboratory and to use his apparatus for this investigation. The result of this work was a very striking one: all of our dyes showing colors of the second order have an exceedingly strong absorption band in the infra-red at a place in the spectrum where other organic and inorganic compounds, even those that are known for their strong absorption of infra-red light, have no absorption at all or only a very slight one. This place is the part of the spectrum which is the nearest to the visible red light about $\lambda = 0.8$ to 1.0μ.

These investigations are far from being concluded, but they have shown clearly the importance of the examination of this part of the spectrum. One special case should be reported here, a case in which the examination of the infra-red spectrum of a dye allows us to draw conclusions as to its constitution.

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[2] Piccard, *Ber.*, 46, 1843 (1913).

Auramine.—The constitution of auramine has often been discussed and quite a number of investigators have been inclined to give to this yellow dye a quinonic formula. If this compound really has a quinonic constitution, it should have a relatively deep color.[3] There has, however, been only one explanation offered as to why auramine, although being quinonic, should be only yellow,—its classification among the colors of the second order. In this case, as can easily be seen, the examination of the infra-red spectrum is the means of deciding the controversy. Our observations show that auramine does not absorb in the infra-red at $\lambda = 0.8$ to 1.0μ, hence it is not a dye of the second order. Therefore, it cannot be quinonic and its constitutional formula[4] is $[(CH_3)_2N—C_6H_4—C(=\mathbf{N}H_2)—C_6H_4—N(CH_3)_2]Cl$.

I wish to thank my collaborator, Dr. L. Marton of Zurich, for his valuable help.

Summary

Our first definition[2] of absorption colors of the second order was as follows: if a compound belongs to a family of colored compounds, the color of which has (as a result of progressive changes) already gone through the ordinary succession from yellow through red and blue to green, and if by further alteration of the molecule in the same sense as the one which had produced this shift of colors we obtain again the same succession of colors beginning with yellow, we call these colors "absorption colors of the second order."

Now, after having studied the infra-red spectrum of numerous dyes of the second order, we can give another and simpler definition: any colored compound has a color of the second order if it has a strong absorption in the infra-red next to the visible part of the spectrum.

Cambridge, Massachusetts

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[3] Semper, *Ann.*, 381, 234 (1911).

[4] We have given up entirely the old-fashioned formulas with quinquivalent nitrogen, chiefly because they are based on an hypothesis without the slightest proof, whereas Werner's coördination formula of ammonium chloride and substituted ammonium chlorides does not pretend anything more than the well-warranted fact that there are in solution two ions, one $[NR_4]$ and one Cl ion. In order to make the formula more lucid we use $\mathbf{N}$ to indicate the nitrogen atom which has saturated its fourth coördination place by addition of the hydrogen ion of the acid (or an alkyl which takes its place). See also Piccard and Dardel, *Helvetica Chim. Acta*, 4, 414 (1921).

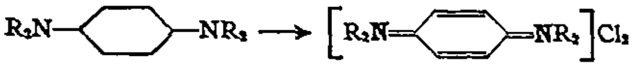
[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 10]

DIMETHYLDIPHENYL-PARA-PHENYLENEDIAMINE AND THE COLOR OF MONO SALTS AND DI SALTS OF HOLOQUINONIC COMPOUNDS

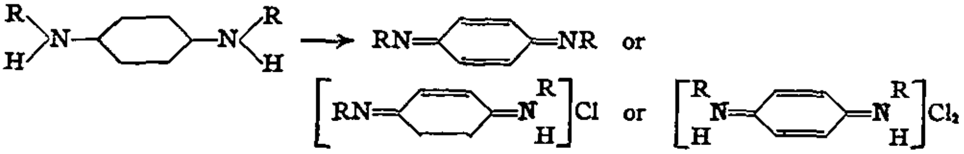
BY JEAN PICCARD

RECEIVED MAY 13, 1926 PUBLISHED SEPTEMBER 4, 1926

If we oxidize any tetrasubstituted phenylenediamine or benzidine to the corresponding holoquinonic salt, we shall always obtain a salt with two molecules of acid, a "di salt."[1]



The above formula shows clearly that it is not possible to obtain either *an imino base or a salt with only one molecule of a univalent acid* ("*mono salt*"). Symmetrically disubstituted phenylenediamines or benzidines, however, may produce on oxidation the free imino base, the mono salt or the di salt.



The salts always have a deeper[2] color than the imino base. While working in this field I found the following interesting and very general rule: quinonedi-imines and diphenoquinonedi-imines (that is, the holoquinonic benzidine derivatives) give mono salts that have a deeper color than the corresponding di salts.

For this reason diphenylbenzidine gives a blue holoquinonic salt and dimethyldiphenylbenzidine, newly prepared by Wieland[3] does not give, as that author expected it to do, a holoquinonic salt of deeper color (for instance, greenish-blue), but it gives a holoquinonic salt of a less deep color, violet-red. This observation induced Wieland to serious doubts of the old law that substitution deepens the color. We were able to show[4] that Wieland had compared the blue color of the mono salt derived from diphenylbenzidine with the color of the salt derived from dimethyldiphenylbenzidine which, of course, must be a di salt. We were able to show that in the case of diphenylbenzidine the holoquinonic mono salt is changed by the addition

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[1] We use the coördination formula; see Ref. 4 in the preceding paper.

[2] In the succession of colors yellow, orange, red, violet, blue, green, each is classed as "deeper" than the preceding one.

[3] Wieland, *Ber.*, 52, 886 (1919).

[4] Piccard, *Helvetica Chim. Acta*, 7, 790 (1924).

of fuming sulfuric acid,[5] its color becomes less deep; it is only violet and there is no doubt that if we could have solutions of the pure di salt, they would be only violet-red.

If our explanation of Wieland's observations is correct, we must confront a similar phenomenon when we compare the holoquinonic salts derived from diphenyl-*p*-phenylenediamine with those derived from dimethyldiphenyl-*p*-phenylenediamine. Since this base has not yet been described, we were obliged to synthesize it. The difficulties that arose showed us why such a relatively simple compound could not be found in the literature.

If the solution of this new base in 95% acetic acid is oxidized, the blue color of the meriquinonic salt[6] first appears and then the color of the holoquinonic salt. It is red, whereas the non-methylated base gives under similar conditions a deeper color, violet-red. By these reactions we have shown that in the phenylenediamine series exactly the same thing happens which had happened in the benzidine series; in acetic acid solution it is the non-methylated holoquinonic salt that has the deeper color, because the non-methylated derivative gives a mono salt and the methylated one must give a di salt.

First Synthesis,[7] $C_6H_5N(CH_3)\boxed{H + I}C_6H_4\boxed{I + H}(CH_3)NC_6H_5$.—A mixture of 16.5 g. of *p*-di-iodobenzene[8] and 32 g. of monomethylaniline was heated 25 hours at 200° to 230° with 85 g. of potassium carbonate and 12 cc. of nitrobenzene in the presence of a few milligrams of catalytic copper.[9] The product of the condensation was isolated as usual. Steam was passed through the reaction mixture which took away any unchanged methylaniline and the nitrobenzene. Then benzene was added and the organic products were separated from the inorganic compounds and the copper powder.

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[5] Kehrmann indicates that azobenzene produces a di salt when dissolved in fuming sulfuric acid. It is certainly correct that fuming sulfuric acid produces a compound which has the color of the di salt, but we doubt that it produces what is really a di salt. The coördinatively only trisubstituted ammonia nitrogen atom is not likely to add hydrogen ions in fuming sulfuric acid if it is not basic enough to do so in concd. sulfuric acid, because in fuming sulfuric acid hydrogen ions are rather few. It seems more likely to pick sulfur trioxide molecules out of the solution. We relate in this connection our observation that many bases which dissolved under salt formation (that is, addition of hydrogen ions) in dil. acetic acid are soluble without salt formation in acetic acid if there is less than 5% of water in it. The solution in glacial acetic acid has on that account the color of the benzene solution of the free base. A small addition of water produces instantaneously the color of the salt because it produces hydrogen ions. It shows that the acetate is not formed by the absorption of acetic acid of which there is plenty in glacial acetic acid, but by absorption of hydrogen ions. It shows also the superiority of the coördination formula for the explanation of salt formation.

[6] See the following paper.

[7] This method for the introduction of phenyl groups into amino groups was invented by F. Ullmann [*Ber.*, **36**, 2838 (1903)]. For further details see Piccard and de Montmollin, *Helvetica Chim. Acta*, **6**, 1016 (1923).

[8] *p*-Dibromobenzene does not react sufficiently.

[9] Piccard, *Helvetica Chim. Acta*, **5**, 147 (1922).

In other cases the evaporation of the benzene solution yielded the desired base in sufficiently pure form to allow further purification by ordinary recrystallization. In this case, however, we obtained only gluey, black mixtures, which gave not even the color reactions that we expected from our new base. In order to extract our dimethyldiphenylphenylenediamine we added to the benzene solution an equal amount of concd. hydrochloric acid. This operation converted all of the bases into hydrochlorides, leaving in the benzene solution only acid or neutral compounds which did not interest us. Both layers were separated and the hydrochloric acid solution was treated with two and one-half times its volume of water. This in turn precipitated the weak bases such as dimethyldiphenylphenylenediamine. These weak bases were again extracted with benzene and the solution was dried and evaporated in a vacuum. A brown, tarry mass was obtained which, however, soon produced crystals of the desired base. These crystals were isolated by pressing the mass on porcelain and then washing them carefully with a few drops of benzene and again with a small amount of alcohol. Dimethyldiphenyl-*p*-phenylenediamine, recrystallized from alcohol, forms colorless prisms which are often 15 to 20 mm. long. It is very soluble in benzene and in alcohol, but only slightly soluble in glacial acetic acid; m. p., 147–151° (corr.).

Anal. Subs., 0.1764: 15.4 cc. of N_2, (17°, 719 mm. (corr., 712)). Calcd. for $C_{20}H_{20}N_2$: N, 9.72. Found: 9.63.

Second Synthesis, $C_6H_5N(CH_3)\boxed{H + HO}C_6H_4\boxed{OH + H}(CH_3)NC_6H_5$.—Calm[10] had prepared diphenyl-*p*-phenylenediamine by heating hydroquinone with aniline in a sealed tube in the presence of calcium chloride and zinc chloride. For the synthesis of our base we replaced the aniline by monomethylaniline. The method gave very poor results and we obtained a base that by oxidation gave a holoquinonic salt, which changed color on the addition of concd. sulfuric acid. We have seen above that the holoquinonic salt derived from dimethyldiphenyl-*p*-phenylenediamine has two quaternary nitrogen atoms and must, therefore, give only one salt, a di salt. For this reason it cannot change color on the addition of a stronger acid. The observed change of color shows that during the condensation some of the methyl groups have migrated into the nucleus. By running the condensation very carefully we could, however, obtain enough dimethyldiphenyl-*p*-phenylenediamine to identify the base with that obtained by the first method. The color of the holoquinonic salt, as expected, does not change on addition of concd. sulfuric acid.

Third Synthesis, $C_6H_5\boxed{I + H}N(CH_3)C_6H_4N(CH_3)\boxed{H + I}C_6H_5$.—This method, starts with a compound that is rather difficult to make and the condensation does not give encouraging results. For these reasons we stopped working on this line.

Fourth Synthesis, $C_6H_5NHC_6H_4NHC_6H_5 + (CH_3)_2SO_4$.—Five-tenths g. of diphenyl-*p*-phenylenediamine was heated on the water-bath during ten minutes with 4 cc. of dimethyl sulfate. After treatment with sodium hydroxide the base was extracted with benzene and purified by conversion into the hydrochloride as described above. This synthesis is by far the best and if the necessary diphenyl-*p*-phenylenediamine is available it is also a very rapid way to make dimethyldiphenyl-*p*-phenylenediamine. The methylation in alkaline solution does not go so well, nor did the methylation by other methods give good results.

Dimethyldiphenylbenzidine

This compound had been prepared by Wieland but by only a single method, the oxidation of methyldiphenylamine. We made two new syntheses of it; first, diphenylbenzidine was methylated with dimethyl sulfate,

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[10] Calm, *Ber.*, 16, 2803 (1883).

and second, *p.p'*-di-iododiphenyl was treated with monomethylaniline. In both cases, we obtained dimethyldiphenylbenzidine which we could identify with the preparation made by Wieland, for the sample of which we wish to thank Professor Wieland.

It gives me great pleasure to acknowledge the valuable help of Dr. R. Bretagne at the University of Lausanne.

Summary

We have described the preparation of dimethyldiphenyl-*p*-phenylenediamine, and its identity was proved by the fact that we obtained the same compound by three different methods. On oxidation it shows the same characteristics as the corresponding benzidine derivative, dimethyldiphenylbenzidine. We have also carried out two new syntheses of this dimethyldiphenylbenzidine.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE PLAUT RESEARCH LABORATORY OF LEHN AND FINK, INCORPORATED]

FURTHER STUDIES ON THE INTRODUCTION OF ALKYL AND ARYL GROUPS INTO THE NUCLEUS OF POLYPHENOLS

BY EMIL KLARMANN

RECEIVED MAY 18, 1926 PUBLISHED SEPTEMBER 4, 1926

The alkyl and aryl substituted derivatives of resorcinol, some of which possess remarkable antiseptic properties, may be obtained by different methods. Thus, benzylresorcinol is prepared either by the direct introduction of the benzyl group into the nucleus of resorcinol or by the reduction of the corresponding *m*-dihydroxybenzophenone. The first way was used by Liebmann[1] who showed that aliphatic alcohols and benzyl alcohols, when heated with resorcinol in the presence of zinc chloride, combine with resorcinol and form the corresponding substitution derivatives. Klarmann[2] effected a substitution of resorcinol by the condensation of benzyl chloride with resorcinol in the presence of aluminum chloride in nitrobenzene solution. It may be mentioned here that Boeseken[3] considers benzyl chloride as unsuitable for the Friedel-Crafts reaction, since it is declared to lead to resinified products. The reduction of the *m*-dihydroxybenzophenone was studied by Hirzel,[4] Dohme[5] and Klarmann.[2] The ketone was obtained by the first two authors by direct condensation of benzoic acid with resorcinol in the presence of zinc chloride, according to

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[1] Liebmann, *Ber.*, **14,** 1842 (1881); Ger. pat. 17,311 (1881).

[2] Klarmann, THIS JOURNAL, **48,** 791 (1926).

[3] Boeseken, *Rec. trav. chim.*, **23,** 98 (1904).

[4] Hirzel, Brit. pat. 222,136 (1925).

[5] Dohme, Brit. pat. 223,190 (1925).

Nencki,[6] while the latter used Hoesch's[7] method of condensing benzonitrile with resorcinol. All reductions were carried out according to Clemmensen.[8] The applicability of this method for the reduction of dihydroxyketones was proved by Johnson and Lane.[9]

It has been mentioned in a previous paper that a high germicidal action was shown by 2,4-dihydroxydiphenylmethane and 2,4-dihydroxydiphenylethane. We were interested in finding the maximum germicidal action in this series of dihydroxydiphenyl hydrocarbons and prepared 2,4-dihydroxydiphenylpropane, which shows a phenol coefficient of 31. This suggests that the maximum germicidal strength is shown by 2,4-dihydroxydiphenylethane (Table I). The *m*-dihydroxydiphenylpropane was prepared similarly to other compounds of this group by condensation of dihydrocinnamic nitrile with resorcinol and subsequent reduction of the resulting *m*-dihydroxydihydrochalcone. The nitrile was obtained by the action of phosphorus pentoxide on dihydrocinnamamide, the dihydrocinnamoyl chloride having been prepared by the action of thionyl chloride on the free acid.

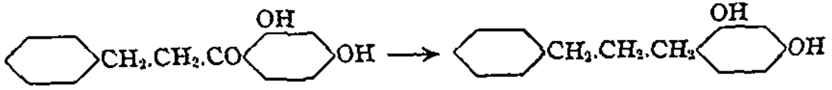
TABLE I

PHENOL COEFFICIENT AND CHEMICAL CONFIGURATION

Resorcinol derivatives				Phloroglucinol derivatives	
Aryl substituent	Ph coeff.	Alkyl substituent	Ph coeff.	Substituent	Ph coeff.
......	0.3	......	0.3	......	≫1
$C_6H_5CH_2$	23	C_2H_5	1.5[a]	C_6H_{13}	8
$C_6H_5C_2H_4$	41	$(C_2H_5)_2$	10	$(C_2H_5)_3$	2.5
$C_6H_5C_3H_6$	31	C_3H_7	4.3[a]	$C_6H_5CH_2$	7.5
		$(C_3H_7)_2$	18	$C_6H_5C_2H_4$	8
		C_4H_9	8[a]	$C_6H_5C_3H_6$	8.8
		$(C_4H_9)_2$	10		
		C_6H_{13}	45[b]		
		$(C_6H_{13})_2$	21		
		$C_{12}H_{25}$	≫1		

[a] Johnson and Lane, Ref. 9.

[b] Leonard, Ref. 14.



All alkyl and aryl substitution products of resorcinol and phloroglucinol that were hitherto tested biologically are monosubstituted derivatives. We were interested in the preparation of disubstituted resorcinol and trisubstituted phloroglucinol derivatives in order to see how the introduction

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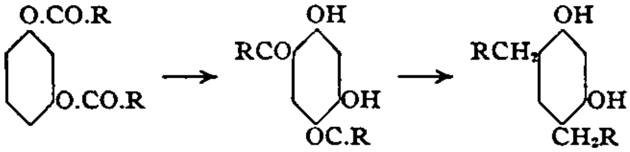
[6] Nencki, *Monatsh.*, 10, 906 (1889).

[7] Hoesch, *Ber.*, 48, 1122 (1915).

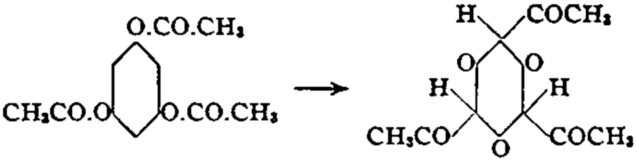
[8] Clemmensen, *Ber.*, 46, 1837 (1913); 47, 687 (1914).

[9] (a) Johnson and Lane, THIS JOURNAL, 43, 348 (1921). (b) Dohme, Cox and Miller, *ibid.*, 48, 1688 (1926).

of further alkyl groups influences the germicidal action. We availed ourselves of a reaction that was studied first by Doebner,[10] then by Eijkman,[11] who found that diesters of resorcinol undergo a rearrangement with formation of phendiones when heated with zinc chloride. The reduction of the latter, according to Clemmensen, would then lead to dialkyl derivatives of resorcinol.



A similar rearrangement was observed by Heller[12] who regards the reaction product in the case of phloroglucinol as a derivative of triketohexamethylene.



The reduction of this product leads, however, to a trialkyl derivative of phloroglucinol. This fact and Heller's arguments, which permit an explanation different from his, likewise make the phenolic structure appear probable.

In all reductions studied, the end of a reduction was indicated by a practically negative reaction of the alcoholic solution of the product to ferric chloride, while all keto compounds gave a very distinct red coloration with ferric chloride.

We prepared diethyl-, dipropyl-, dibutyl-, dihexyl- and dodecylresorcinol and triethylphloroglucinol. Actually, it is shown in some cases that the phenol coefficient of disubstituted derivatives is several times higher than that of a corresponding monosubstituted compound. In other cases it is lower. Besides, the total weight of side chains may be higher in a disubstituted resorcinol than in a monosubstituted and still a powerful germicidal compound results. Thus dihexylresorcinol shows a phenol coefficient of 21, while dodecylresorcinol is practically inactive. (Table I.)

The dialkyl derivatives of resorcinol were prepared from the corresponding esters and the latter were obtained by heating resorcinol with a small excess of the respective acid chloride. Dodecylresorcinol was prepared by the reduction of lauroresorcinol; the latter results on condensation of resorcinol with lauric acid in the presence of zinc chloride.

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[10] Doebner, *Ann.*, **210**, 259 (1881). Nencki and Sieber, *J. prakt. Chem.*, [2] **23**, 149 (1881).

[11] Eijkman, *Chem. Weekblad*, **2**, 59, 79 (1905).

[12] Heller, *Ber.*, **42**, 2736 (1909).

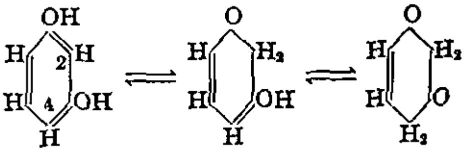
Attempts have also been made to prepare compounds that contain halogen in the side chain. While keto compounds of resorcinol are readily obtained, those of phloroglucinol lead immediately to coumaranone derivatives of the type observed by Sonn,[13] even when the halogen does not stand at the end of the side chain as in Sonn's experiments. The boiling with hydrochloric acid, however, partly eliminates the halogen of the halogen alkylresorcinol derivatives, and products of a changing composition result.

The phenol coefficients were determined according to the method of the Hygienic Laboratory. Since some substances are very difficultly soluble in water, the original emulsion was prepared by adding distilled water to the alcoholic solution of the tested substance. The further dilutions, however, were made with water so that not more than 1% of alcohol was present in the sample on which the final reading was made.

Conclusion

While hexylresorcinol possesses the maximal germicidal action among the mono-alkyl derivatives of resorcinol, according to Johnson and collaborators, and Leonard *m*-dihydroxydiphenylethane seems to be the strongest among the mono-aryl derivatives of resorcinol. Introduction of two alkyl groups into the nucleus of resorcinol in some cases leads to compounds with a stronger germicidal action than that of the mono-alkyl derivatives, while in other cases weaker compounds are obtained. The germicidal strength of phloroglucinol may be similarly increased, all three compounds of the trihydroxydiphenyl hydrocarbon series having approximately the same phenol coefficient while triethylphloroglucinol is weaker than hexylphloroglucinol.[14]

The experiments carried out hitherto allow an explanation for these phenomena to be attempted. We may assume that the antiseptic action of phenols is due to the presence of the hydroxyl groups. On the other hand, it appears from different investigations that a keto structure may be ascribed to many unsubstituted polyphenols.



We assume further that, of the tautomeric forms, the keto form does not possess an antiseptic action. It follows from Werner's theory of the changing valence of the carbon atom that the valence with which a radical is attached to a carbon atom varies with various radicals. If we combine this assumption with that of the dynamic keto structure previously men-

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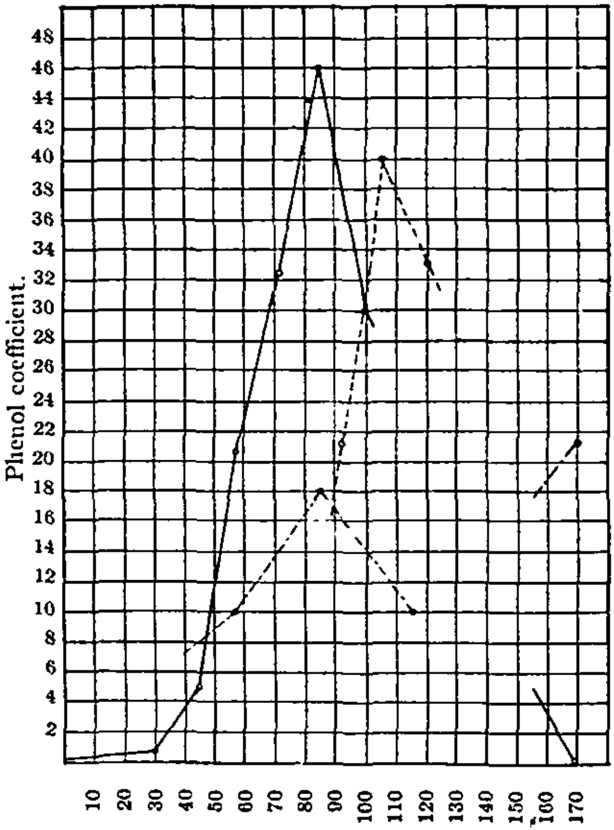
[13] Sonn, *Ber.*, 50, 1262 (1917).

[14] Klarmann and Figdor, THIS JOURNAL, 48, 803 (1926).

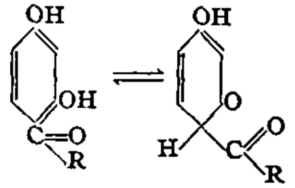
tioned, it follows that the carbon atoms of Positions 2 and 4 will be the less receptive for the hydrogen atom of the hydroxyl groups of Positions 1 and 3, the more their valence is engaged in binding an alkyl group. Thus the shift of the hydrogen atom is made increasingly improbable with the increasing weight of the side chains. This does not mean that the unsubstituted resorcinol is assumed to possess the tautomer keto structure under normal conditions, but rather that this configuration may form in the medium in which the processes take place that summarily appear as antiseptic action.



The relationship between the weight of the side chain and the phenol coefficient. ———Full line; alkyl derivatives of resorcinol (Johnson and Lane, Leonard). - - - -Dash line; aryl derivatives of resorcinol. -—-—Dash and dotted line; dialkyl derivatives of resorcinol.

It is perhaps significant in this connection that none of the alkyl and aryl substituted compounds studied gives a pronounced color reaction with ferric chloride, while the unsubstituted resorcinol and phloroglucinol give characteristic colorations. In the case of monosubstituted derivatives the resemblance of the *ortho* and *para* positions of the hydroxyl groups in relation to the substituting group is to be considered.[14a]

The weakening of the germicidal action on introduction of acyl groups is explainable by considering the possibility of the equilibrium.



In a similar sense the hydroxyl group in *para* position to the keto group might be influenced. The same ideas refer likewise to other phenols. It is, however, not clear why the limit of bactericidal action is reached with a side chain of comparatively few carbon atoms, unless we assume that the solubility in the substance in which the antiseptic action takes place, is entirely changed.

Leonard[15] states that the antiseptic power of mono-alkyl derivatives of resorcinol is due to their ability to lower the surface tension. Therefore the compounds penetrate more easily through the membranes. It is possible that the germicidal action is due to a combination of the physical ability to lower the surface tension with the chemical ability to increase the reactivity of the hydroxyl group as outlined before.

Experimental Part

Preparation of 2',4'-Dihydroxy-α,β-dihydrochalcone, $C_6H_5.CH_2.CH_2.CO.C_6H_3(OH)_2$ and of 2,4-Dihydroxydiphenylpropane, $C_6H_5.CH_2.CH_2.CH_2.C_6H_3(OH)_2$.—Forty g. of hydrocinnamic acid and 60 g. of thionyl chloride were heated in a water-bath under a reflux condenser for three hours at 60–70°. The excess of thionyl chloride was removed by evacuation at room temperature. The crude chloride was applied directly for the preparation of the amide.

The hydrocinnamoyl chloride was allowed to drop into a stirred 26% aqueous solution of ammonia which was cooled below 0°. The hydrocinnamamide crystals separated soon and were filtered under suction, washed with water and dried in a vacuum desiccator at room temperature; m. p., 97°; yield, 75%.

Anal. Calcd. for $C_9H_{11}ON$: N, 9.40. Found: 9.26.

The hydrocinnamamide was mixed with phosphorus pentoxide and heated in a vacuum of 65 mm., whereupon the hydrocinnamic nitrile distilled at 170°. This was

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[14a] The introduction of one or more halogen atoms into the nucleus of phenol and and related compounds considerably increases their germicidal action, but at the same time reduces their reactivity in the presence of proteins [Bechhold and Ehrlich, *Z. physiol. Chem.*, 47, 175 (1906).]

This is probably due to the increased electrolytic dissociation of the halogen substituted compound (that is, the more pronounced acid nature of the OH group). In contrast to this phenomenon, it is assumed that in the case of alkyl or aryl substitution the pratically undissociated form of the phenols is to be considered in the keto-enol equilibrium as outlined before.

[15] Leonard and Wood, *J. Am. Med. Assoc.*, 85, 24, 1855 (1925).

shaken with concd. potassium carbonate solution, filtered, dried with phosphorus pentoxide and redistilled in a vacuum; yield, 40%.

The condensation with resorcinol was carried out in the following way. Twenty-seven g. of the nitrile and 22 g. of resorcinol were dissolved in 100 cc. of dry ether, 6 g. of fused and powdered zinc chloride was added and a current of dry hydrogen chloride was allowed to pass through the mixture for three and one-half hours. The oily residue was allowed to stand in the ice box overnight, then cold hydrochloric acid (1 : 1) was added. On rubbing and shaking, the keto-imido hydrochloride separated in small crystals which were filtered off and washed with ether. By boiling with water for 25 minutes, the 2',4'-dihydroxy-α,β-dihydrochalcone was precipitated. When sufficient water was present, silky needles were obtained. After being washed and dried in air, they melted at 84° (uncorr.); yield, about 50% of the nitrile. It gave a dark red coloration with ferric chloride in alcoholic solution. The substance contains 1 molecule of water of crystallization; the drying of the analysis sample was effected out in a microvacuum desiccator.

All combustions were carried out according to the micro method of Pregl; samples of 3–5 mg. were taken.

Anal. Calcd. for $C_{15}H_{14}O_3.H_2O$: H_2O, 6.92. Found: 6.44.

Calcd. for $C_{15}H_{14}O_3$: C, 74.35; H, 5.82. Found: C, 74.26; H, 5.91.

This compound was reduced with amalgamated zinc and 1: 3 hydrochloric acid in the usual way. The reduction product was shaken out with ether; the ether was evaporated after drying and the residue was allowed to stand with half of its volume of benzene in the ice box overnight. A crystalline mass was formed which was filtered and washed with a mixture of one part of benzene and two parts of petroleum benzine and dried in a vacuum at room temperature; m. p., 70–71° (uncorr.); yield, about 50% of the keto compound. Ferric chloride produces a precipitate after some time; the phenol coefficient is 31.

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.91; H, 7.06. Found: C, 79.45; H, 7.41.

Preparation of 2',4',5'-Trihydroxy-α,β-dihydrochalcone, $C_6H_5CH_2.CH_2.CO.C_6H_2(OH)_3$ and of 2,4,6-Trihydroxydiphenylpropane, $C_6H_5.CH_2.CH_2.CH_2.C_6H_2(OH)_3$.—The condensation of hydrocinnamic nitrile with phloroglucinol was carried out in the way that was described before. The weights taken were 13 g. of the nitrile and 12.5 g. of phloroglucinol. The method of isolation was the same; m. p. of the air-dried trihydroxydihydrochalcone, 140° (uncorr.). It gave a red coloration with ferric chloride in alcoholic solution. The compound contains 1 molecule of water of crystallization.

Anal. Calcd. for $C_{15}H_{14}O_4$: C, 69.74; H, 5.46. Found: C, 69 21; H, 5.41.

Calcd. for $C_{15}H_{14}O_4.H_2O$: H_2O, 6.52. Found: 6.83.

The reduction was carried out with amalgamated zinc and 5% hydrochloric acid. The product was isolated with ether, recrystallized from benzene and dried in a vacuum; m. p., 80–81° (uncorr.). On standing, a precipitate with ferric chloride forms; phenol coefficient, 8 8.

Anal. Calcd. for $C_{15}H_{16}O_3$: C, 73.77; H, 6.60. Found: C, 73.23; H, 7.05.

Preparation of the Di- and Trisubstituted Phenols

In general the following procedures were used to carry out the three steps in the preparation of the substituted phenol.

Esterification.—The polyphenol was heated under a reflux condenser with a small excess of the acid chloride for two to three hours at 70–75°. The resulting product was shaken with water, extracted with ether and, after evaporation of the latter, subjected to fractional distillation.

Rearrangement.—The rearrangement of the esters was carried out in general by heating to 130° with zinc chloride (previously fused and powdered). This melt was allowed to cool during stirring and addition of methanol. The resulting product, which usually crystallized, was filtered off and recrystallized from an appropriate solvent. The yields were 40–50% based on the ester.

Reduction.—The rearrangement product was reduced by the method of Clemmensen using zinc amalgam and 1:2 or 1:3 hydrochloric acid. The liquefied rearrangement product was reduced during 16 to 24 hours, the reduced compound isolated by means of ether and recrystallized from

Table II

Experimental Data on the Alkyl and Aryl Compounds

R = Resorcinol derivative. P = Phloroglucinol derivative

		M. p., °C. (uncorr.)	B. p., °C.	*P*, mm Hg	Analyses			
					C		H	
					Calcd.	Found	Calcd.	Found
			Esters					
R	Dibutyrate		195–200	18	67.19	7.23	66.73	8.03
R	*Dicaproate*		*210–220*	*12*	*70.57*	*8.56*	*70.32*	*9.07*
			Acyl Compounds					
R	Diaceto[11]	182						
R	Dipropio[16]	125						
R	Dibutyro	64–65			67.18	7.76	66.46	8.26
R	Dicapro		215–220	6	70.15	8.56	70.19	9.16
R	Lauro	79–80			73.92	9.65	73.50	9.23
						Br		Br
R	*α-Bromobutyro*	*114–115*				*30.87*		*29.84*
P	Tri-aceto[a]							
			Alkyl Compounds					
R	Diethyl	71			71.29	8.42	72 38	8.90
R	Dipropyl	59			74.19	9.28	73 35	9.19
R	Dibutyl[c]	. ...	194–196	14	75.61	10.0	73.36	11.79
R	Dihexyl		205	7	77.68	10.87	76.96	11.29
R	Dodecyl	65–66			77.86	10.86	77 81	11.12
P	Tri-ethyl[b]	126			68.54	8.54	68.22	8.73

[a] Acetic anhydride and sodium acetate were used to prepare the phloroglucinol triacetate instead of acetyl chloride as suggested by Hlasiwetz [*Ann.*, 119, 201 (1861)]. The latter method gives poor yields. Ten g. of phloroglucinol, 50 g. of acetic anhydride and 6 g. of sodium acetate were boiled for two hours on a sand-bath. The excess of the acid anhydride was removed with 20 cc. of water; on cooling, the compound crystallized.

[b] The reduction of the triacetophloroglucinol was carried out in amyl alcohol using zinc amalgam and 1 : 5 hydrochloric acid. The mixture was boiled for 24 hours. The compound was isolated from the amyl alcohol layer with 5% sodium hydroxide solution. The sodium hydroxide extract was then acidified, extracted with ether and after evaporation of the latter, recrystallized from a little benzene.

[c] The dibutylresorcinol could not be obtained in crystalline form. The product was purified by vacuum distillation. Judging from the analysis it is not entirely pure.

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[16] Wittig, *Ber.*, 59, 117 (1926).

an appropriate solvent. The yield of the reduction product varied from about 30–60% of the keto compound. The experimental data on the series of compounds prepared by the above method are contained in Table II.

Preparation of 1,3-Dihydroxy-4-laurophenone, $C_6H_3(OH)_2(CO.C_{11}H_{23})$, **and of 1,3-Dihydroxy-4-dodecylbenzene (dodecylresorcinol),** $C_6H_3(OH)_2.C_{12}H_{25}$.—Twenty-four g. of lauric acid and 10 g. of zinc chloride were heated on a sand-bath until most of the zinc chloride dissolved. The mixture was allowed to cool to 100° and 5 g. of resorcinol was added. Then the flask was heated slowly to 250°. The cooled, solidified mass was remelted, poured into water at 80° and stirred vigorously. The cooled mixture was shaken with ether. The crystalline precipitate of zinc laurate was suspended in the ethereal solution and then filtered off, the ether evaporated and the residue distilled in a vacuum. The fraction distilling at 260–265° (8 mm.) was collected as a heavy, yellow oil that solidified on standing. It was recrystallized thrice from ligroin and formed greasy plates; m. p., 79–80° (uncorr); yield, 55% of the resorcinol; m. p. of zinc laurate, 129°.

Anal. Calcd. for $C_{18}H_{28}O_3$: C, 73.92; H, 9.65. Found: C, 73.50; H, 9 23.

Calcd. for $C_{12}H_{23}O_2Zn$: Zn, 15.70. Found: 15.44.

Five g. of the keto compound was heated with amalgamated zinc and 1:2 hydrochloric acid for 16 hours under a reflux condenser. A distinct swelling took place and in a short time a jelly-like mass filled a volume of about 300 cc. This voluminous mass falls apart in the cold. Therefore, the heating must be interrupted from time to time. The product was extracted with ether and recrystallized from petroleum benzene; it gave shiny plates; m. p., 65–66°.

Anal. Calcd. for $C_{18}H_{30}O_2$: C, 77.86; H, 10.86. Found: C, 77.81; H, 11.12.

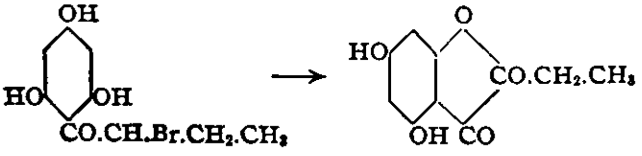
Preparation of 1,3-Dihydroxy-α-bromobutyrophenone-4, $C_6H_2(OH)_2CO.CHBr.CH_2.CH_3$.—The crude product of bromination of butyric acid was kept in a vacuum at room temperature in order to remove the excess of hydrobromic acid and the liquid was then allowed to drop into a cold ammonia solution during stirring, in the shortest time possible. The amide formed was filtered off and washed quickly, dried in a vacuum and distilled with phosphorus pentoxide. The resulting nitrile was purified with potassium carbonate and redistilled.

The condensation, according to Hoesch, was carried out as usual. Equimolecular parts of bromobutyric nitrile and resorcinol were dissolved in ether and a current of dry hydrogen chloride was allowed to pass through the mixture. The keto-imido hydrochloride was isolated and boiled with water for ten minutes. It separated in needles which, after being dried in a vacuum, melted at 114–115° (uncorr.) and gave a red coloration with ferric chloride.

Anal. Calcd. for $C_{10}H_{10}O_3Br$: Br, 30.87. Found: 29.84.

The low bromine content indicates that bromine was split off to a minor extent on boiling with water. No uniform product results when the reduction is attempted.

Preparation of 1-Ethyl-3,5-dihydroxycoumaranone-2.—This compound is obtained when the condensation product of bromobutyric nitrile and phloroglucinol is boiled with water. It probably forms according to the reaction



It is obtained from water in crystalline aggregates; m. p., 165–166° (uncorr.), giving an intense violet coloration with ferric chloride.

Anal. Calcd. for $C_{10}H_{10}O_4$: C, 61.84; H, 5.20. Found: C, 61.75; H, 5.76.

Mol. wt. (Rast[17]) Subs., 0.0210 g. in 0 2759 g. of camphor: Δt, 14°. Calcd. for $C_{10}H_{10}O_4$: mol. wt., 194. Found: 222.5.

My thanks are due to Mr. E. Tilly who carried out the determinations of the phenol coefficients according to the method of the Hygienic Laboratory.

Summary

In order to obtain more data on the influence of introduction of aryl and alkyl groups into the nucleus of polyphenols on the germicidal action, a number of new compounds were prepared and their phenol coefficients determined. Methods are given for the preparation of *m*-dihydroxydiphenylpropane, *m*-trihydroxydiphenylpropane, diethyl-, dipropyl-, dibutyl-, dihexyl- and dodecylresorcinol and triethylphloroglucinol and the corresponding mono-, di- and triketo compounds from which they are derived. The antiseptic actions of these compounds and their dependence upon the introduced side chains are discussed and a chemical explanation is attempted. Halogen alkyl compounds could not be obtained since the halogen is either split off when the reduction of the keto compound is attempted or a coumaranone derivative forms when the keto-imide is to be transformed into the ketone.

Bloomfield, New Jersey

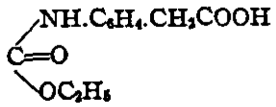
[Contribution from the Chemical Laboratory of the University of Saskatchewan]

STUDIES IN URETHANS. II. ISOMERIC URETHAN DERIVATIVES OF PHENYLACETIC ACID, AND SOME RELATED COMPOUNDS

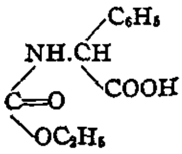
By S. Basterfield and Harold N. Wright

Received May 20, 1926 Published September 4, 1926

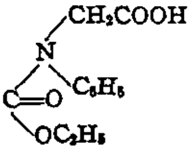
This study was undertaken in order to compare the physiological action of the three isomeric urethans, *p*-carbethoxy-aminophenylacetic acid (I), *dl*-α-carbethoxy-aminophenylacetic acid (II), and N-carbethoxyphenylglycine (III).



I



II



III

Urethans in general are depressing to the central nervous system, and some of those containing aromatic radicals are antipyretic (for ex-

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[17] Rast, *Ber.*, 55, 1051 (1922).

ample, phenylurethan, *p*-ethoxy-phenylurethan). Another effect that may be related to some extent to the antipyresis is a diminution in tone and rhythmic movement of involuntary muscle in a variety of tissues.[1]

The last effect might well be expected in Substances I and II since they contain substituted benzyl groups in addition to the urethan group. While the carboxyl group might tend to offset the expected properties, it affords the opportunity of converting the compounds into alkali salts or esters at will, and of producing corresponding changes in the solubility relations of the compounds.

Preliminary experiments with some of the compounds prepared have been carried out on rabbits. No well-defined systemic effects have been obtained. The compounds seem to be non-toxic and generally inert. Detailed studies now in progress, especially on the action on smooth muscle tissues, will be reported elsewhere.

Experimental Part

_p_-Carbethoxy-aminophenylacetic Acid, $C_2H_5O.OC.NH.C_6H_4.CH_2.COOH$.—This was prepared by dissolving 5 g. of *p*-aminophenylacetic acid in a slight excess of sodium hydroxide solution and adding the calculated amount of ethyl chlorocarbonate during vigorous shaking and cooling. A heavy, pale yellow precipitate was formed, the reaction being complete in 15 to 20 minutes. The product was dissolved in dil. sodium hydroxide solution and reprecipitated with hydrochloric acid. Colorless crystals were obtained; m. p., 125°; yield, 93%. The acid is only slightly soluble in water.

Anal. Calcd. for $C_{11}H_{13}NO_4$: N, 6.28. Found: 6.34.

SODIUM SALT.—The acid was dissolved in an excess of sodium hydroxide, the solution made exactly neutral, and evaporated to dryness on the hot-plate at 60–65°. The solid residue was extracted with alcohol and the solution filtered. From the concentrated alcoholic solution, colorless crystals separated. They sintered at 168–170°; yield, 60–65%.

The ester was obtained in a 92% yield by heating an absolute alcoholic solution of the acid with dry hydrogen chloride, and allowing the mixture to stand in the ice box overnight. A heavy white precipitate was obtained, which after recrystallization from alcohol melted at 80°.

Anal. Calcd. for $C_{13}H_{17}NO_4$: C, 62.15; H, 6.77; N, 5.58. Found: C, 61.91; H, 6.57; N, 5.57.

During the course of this experimental work both the ester and the carbethoxy-amino acid were hydrolyzed in alkaline solution. After the reaction mixture had been heated for half an hour or so, and the liquid neutralized with acid, a small amount of white, gelatinous precipitate was obtained, which was filtered off. The filtrate was evaporated to dryness and the residue extracted with alcohol. The alcoholic solution yielded glassy, brownish crystals of the sodium salt of *p*-aminophenylacetic acid, containing alcohol of crystallization. The crystals melted at 69° and after being kept in a desiccator over sulfuric acid effloresced to a brown powder; m. p., 130–135°.

If the hydrolysis was prolonged, it was found that larger and larger amounts of the white gelatinous material were obtained and smaller quantities of the sodium salt of the amino acid.

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[1] Franklin, *J. Pharmacol.*, 26, 227 (1925).

Ethylation of *p*-Carbethoxy-aminophenylacetic Ethyl Ester

Attempts were made to ethylate the alpha carbon atom of the ester by the usual method with sodium and ethyl iodide in absolute alcoholic solution, but without success. The ester was always recovered unchanged.

Ethylation of the nitrogen of the carbethoxy-amino group was moderately successful by the use of diethyl sulfate.

Ammonium Salt of *p*-Carbethoxy-ethylaminophenylacetic Acid, $C_2H_5OOC.N(C_2H_5).C_6H_4.CH_2.COONH_4$.—To 4 g. of the ester dissolved in 50 cc. of absolute alcohol was slowly added 8 cc. of diethyl sulfate. The mixture was shaken and warmed to 60° during the operation, after which it was refluxed for one hour. Twenty-five cc. of concd. ammonium hydroxide was added to destroy unchanged diethyl sulfate, and the mixture allowed to stand overnight in the ice chest. A precipitate of unchanged ester was filtered off, and the filtrate concentrated and strongly cooled. Crystals were obtained that melted at 99–100°. They were very soluble in water and evolved ammonia on being warmed with alkali.

Anal. Calcd. for $C_{13}H_{20}N_2O_4$: N, 10.46. Found: 10.54.

_dl_-α-Carbethoxy-aminophenylacetic Acid, $C_6H_5.CH(NHCOOC_2H_5)-COOH$.—The amino group of the α-aminophenylacetic acid appeared at first to be very unresponsive to the action of ethyl chlorocarbonate. When the two compounds were refluxed together there was no sign of reaction. This may have been due to the insolubility of the acid in the ester. The reaction was found to proceed slowly but fairly completely in an aqueous medium.

Four g. of the acid was dissolved in 13 cc. of 10% sodium hydroxide solution and 150 cc. of water was added. The calculated amount of ethyl chlorocarbonate was added in small portions during thorough shaking. After several hours a pale yellow oil separated and was extracted with ether. After removal of the ether by evaporation, the oil was cooled in a freezing mixture but failed to solidify. It was found in a subsequent preparation that the oil solidified when allowed to stand in contact with the aqueous reaction medium for 48 hours in the ice chest. The solid was recrystallized from alcohol and gave small, colorless crystals; m. p., 121–122°; yield, 80%.

Anal. Calcd. for $C_{11}H_{13}NO_4$: N, 6.28. Found: 6.35.

SODIUM SALT.—This was prepared by dissolving the acid in a slight excess of sodium hydroxide, making the solution exactly neutral and evaporating to dryness. The residue was extracted with alcohol and the extract concentrated. As the salt failed to crystallize, the solution was cooled in a freezing mixture and 15–20 volumes of ether was added. After 12 hours in the ice box, a white precipitate of the salt was obtained. Precipitation continued for five or six days. The product consisted of fine, colorless crystals that sintered at 210° and decomposed with effervescence at 220–225°.

Anal. Calcd. for $C_{11}H_{12}NO_4Na$: N, 5.72. Found: 5.61.

N-Carbethoxy-N-phenylglycine, $C_2H_5OOC.N.(C_6H_5).CH_2.COOH$.—This was prepared according to the method of Leuchs and Manasse[2] in somewhat similar manner to the α-carbethoxy-amino acid described above.

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[2] Leuchs and Manasse, *Ber.*, 40, 3235 (1907).

SODIUM SALT.—This was prepared in the same manner as the salt of α-carbethoxyaminophenylacetic acid. It gave small crystals, easily soluble in water and in 90–95% alcohol and only slightly soluble in absolute alcohol; yield, 45%; m. p., 227°.

Anal. Calcd. for $C_{11}H_{12}NO_4Na$: N, 5.72. Found: 5.81.

p-Carbethoxy-aminobenzoic Acid, $C_2H_5OOC.NH.C_6H_4.COOH$.—This and its ethyl ester were prepared in order that their physiological actions might be compared with those of the corresponding phenylacetic acid compounds. *p*-Aminobenzoic ethyl ester has local anesthetic properties and it seemed likely that its carbethoxy derivative would have similar properties, while the corresponding phenylacetic compound should not, if Kamm's generalization[3] is true.

Three g. of *p*-aminobenzoic ethyl ester was refluxed with sodium hydroxide until saponification was complete. The solution was almost neutralized with hydrochloric acid, the calculated amount of ethyl chlorocarbonate was added and the mixture was shaken and cooled. A heavy, pink precipitate was formed. The product was dissolved in sodium hydroxide solution and reprecipitated with hydrochloric acid. The crystals were faintly pink, m. p., 201°; yield, 95%.

Anal. Calcd. for $C_{10}H_{11}NO_4$: N, 6.70. Found: 6.61.

p-Carbethoxy-aminobenzoic Ethyl Ester, $C_2H_5OOC.NHC_6H_4.COOC_2H_5$.—A solution of 3 g. of *p*-aminobenzoic ethyl ester in 75 cc. of ether was shaken with 6 cc. of ethyl chlorocarbonate in the presence of 20 cc. of 10% sodium hydroxide solution. After two hours the ether layer was evaporated and the solid residue recrystallized from alcohol; m. p., 130°; yield, 84%.

Anal. Calcd. for $C_{12}H_{15}NO_4$: N, 5.91. Found: 5.97.

Summary

1. The preparation of isomeric urethan derivatives of phenylacetic acid and some related compounds is described.

2. The following new compounds were prepared: *p*-carbethoxy-aminophenylacetic acid, and its sodium salt and ethyl ester, *dl*-α-carbethoxy-aminophenylacetic acid and its sodium salt, the sodium salt of N-carbethoxy-phenylglycine, *p*-carbethoxy-aminobenzoic acid and its ethyl ester, the ammonium salt of *p*-carbethoxy-ethylaminophenylacetic acid.

3. No definite systemic effects have been observed in the preliminary pharmacological study of these compounds.

SASKATOON, CANADA

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[3] Kamm, THIS JOURNAL, 42, 1030 (1920).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF SASKATCHEWAN]

STUDIES IN URETHANS. III. THE PREPARATION OF VARIOUS SUBSTITUTED URETHANS

BY S. BASTERFIELD, ESLI L. WOODS AND HAROLD N. WRIGHT

RECEIVED MAY 20, 1926 PUBLISHED SEPTEMBER 4, 1926

As part of a study of the chemistry and pharmacology of urethans, a number of substituted urethans have been prepared in this Laboratory, and it seemed desirable to record those that have not previously been described in the literature, and to describe improved or modified methods of preparation for some that have been reported already.

These compounds have been prepared (1) by treating a solution of an amine in ether or benzene with the required amount of alkyl chlorocarbonate in the presence of an aqueous solution of sodium or potassium hydroxide, or (2) by heating together an amino compound and an alkyl chlorocarbonate with or without a solvent, or (3) by heating together a urethan with an acid chloride with or without a solvent.

Preliminary observations on the pharmacological properties of some of these compounds are included in this paper but detailed studies will be reported elsewhere.

Experimental Part

Acetylphenylurethan, $CH_3CO.N(C_6H_5).COOC_2H_5$.—This has been prepared by Sanders[1] and Nijk,[2] both of whom acetylated phenylurethan with a mixture of acetyl chloride and acetic anhydride. The second named worker also obtained it by the action of ethyl chlorocarbonate on the sodium salt of acetanilide.

In the present study an attempt was made to acetylate phenylurethan in ether solution by the action of acetyl chloride in the presence of aqueous alkali, but without success. The acetylation as carried out by Sanders and Nijk gave the most satisfactory results. The urethan was obtained as a colorless oil boiling at 142° at 10 mm. pressure; yield, 85–90%.

Anal. Calcd. for $C_{11}H_{13}NO_3$: N, 6.77. Found: 6.91.

The oil was quite viscous when first obtained, but after standing some months in a sealed tube it became considerably more mobile.

For a comparative pharmacological study two isomers of this urethan were prepared, namely, phenylacetylurethan and *p*-acetylphenylurethan.

Phenylacetylurethan, $C_6H_5CH_2.CO.NHCOOC_2H_5$.—This was obtained by heating equimolecular proportions of urethan and phenylacetyl chloride together under a reflux condenser at 60–70° until hydrogen chloride ceased to be evolved. This took several days, as the mixture became solid and had to be broken up frequently. Better results were obtained

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[1] Sanders, THIS JOURNAL, 22, 378 (1900).

[2] Nijk, *Rec. trav. chim.*, 39, 699 (1920).

by heating the urethan and acid chloride in boiling benzene; the reaction was complete in 16 to 24 hours. The product was recrystallized from hot alcohol or ligroin (b. p., 60–90°) and formed soft, white needles; m. p., 113°; yield, 70%.

Anal. Calcd. for $C_{11}H_{13}NO_3$: N, 6.77. Found: 6.61, 6.76.

***p*-Acetylphenylurethan,** $CH_3CO.C_6H_4.NHCOOC_2H_5$ (*p*-carbethoxyamino-acetophenone) is reported by Nijk[2] to be produced when *p*-amino-acetophenone and potassium hydroxide are dissolved in hot alcohol, treated with ethyl chlorocarbonate dissolved in ether, and the mixture refluxed for an hour. Several attempts to obtain the urethan by this method failed. Most of the product obtained was alkali carbonate, a result that might be expected under the conditions described, since the *p*-amino-acetophenone is not very reactive, and would not be likely to react appreciably with the chlorocarbonate with strong alkali present in the same phase.

The *p*-amino-acetophenone was dissolved in ether and a concentrated aqueous solution of sodium or potassium hydroxide added as a second phase. The calculated amount of ethyl chlorocarbonate was added in small quantities during vigorous shaking to ensure thorough mixing of the two phases. The ether layer was dried over sodium sulfate and evaporated. The solid obtained was recrystallized from alcohol and melted at 158°, as reported by Nijk; yield, 48%.

A better yield was obtained by the direct action of ethyl chlorocarbonate on *p*-amino-acetophenone without any solvent present. There was no action when the two were mixed in the cold, but on being warmed they reacted vigorously. The reaction was complete in a few minutes and the excess of ester was driven off in a current of air. The yield was practically quantitative.

Anal. Calcd. for $C_{11}H_{13}NO_3$: N, 6.77. Found; 6.80.

Benzylurethan, $C_6H_5CH_2.NH.COOC_2H_5$ (ethylbenzylcarbamate).—Benzylamine in ether solution was treated with ethyl chlorocarbonate (one molecular proportion) added in small quantities, and the whole shaken with aqueous alkali after every addition. The ether solution was separated and dried, and the ether distilled. The urethan was left as a colorless oil of slight aromatic odor. It distilled with slight decomposition at 230°. The substance remained liquid for about two weeks and then suddenly solidified to a mass of white needles. After recrystallization from ether at 5° the substance melted at 44°; yield, 80–90%.

Anal. Calcd. for $C_{10}H_{13}NO_2$: N, 7.82. Found: 7.88, 7.72.

***p*-Bromophenylurethan,** $BrC_6H_4.NH.COOC_2H_5$.—This was prepared from *p*-bromo-aniline by the method described above. The reaction was slow. The substance was recrystallized from ligroin (b. p., 60–90°), and melted at 85°; it formed long, thin needles; yield, almost 100%.

Anal. Calcd. for $C_9H_{10}NBrO_2$: N, 5.7. Found: 5.5.

***p*-Iodophenylurethan,** $IC_6H_4.NHCOOC_2H_5$.—This was prepared in similar manner from *p*-iodo-aniline. The reaction was more vigorous than with the bromo-aniline, but much slower than with unsubstituted aniline. The product crystallized in small needles from ligroin; m. p., 116°; yield, 90%.

Anal. Calcd. for $C_9H_{10}NIO_2$: N, 4.8. Found; 4.6.

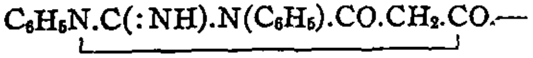
Malonyldiphenyldiurethan, $CH_2(CO.N(C_6H_5).COOC_2H_5)_2$.—This compound was prepared by heating together malonyl chloride and phenylurethan (two molecular proportions) at 50–60° for about a week. Hydrogen chloride was slowly evolved and a brown viscid liquid was produced which slowly deposited crystals after cooling. The mass was worked up with cold alcohol and the solid obtained filtered off and recrystallized from hot alcohol. An alternative method of separation was to add ether to the viscid product until no further precipitation occurred. The precipitate was a brown, amorphous solid which was rejected. The ether solution was evaporated, leaving a residue of oil and crystals. The latter were separated by filtration, and the adhering oil was washed away with cold alcohol. The pure product consisted of white needles; m. p., 123–124°. The yield was very small.

Anal. Calcd. for $C_{21}H_{22}N_2O_6$: N, 7.03. Found: 6.75.

Malonyl-dibenzyl-diurethan, $CH_2(CON(CH_2C_6H_5).COOC_2H_5)_2$.—This was prepared in the manner described above from benzylurethan. The reaction was much more vigorous than with phenylurethan. The reddish, viscid liquid that was formed, solidified slowly to an orange mass. After recrystallization from dilute alcohol, the compound appeared as white needles melting at 75°; yield, 36%.

Anal. Calcd. for $C_{23}H_{26}N_2O_6$: N, 6.57. Found: 6.68.

1,3-Diphenyl-2-iminobarbituric Acid,



$$\underbrace{C_6H_5N.C(:NH).N(C_6H_5).CO.CH_2.CO}$$—

Although this is not a urethan, it is described here because it was prepared in connection with the study of malonyl diurethanes. Diphenylguanidine was dissolved in ether and treated with malonyl chloride (1 molecular proportion) in the presence of aqueous potassium hydroxide. The reaction was quite vigorous and the mixture was cooled in water from time to time. The product was obtained as a brownish solid from the ether. It was recrystallized from a mixture of alcohol and ligroin; m. p., 148°; yield, 76%.

Anal. Calcd. for $C_{16}H_{13}N_3O_2$: N, 15.05. Found: 14.93.

Diphenyl-ethylene-diurethan, $(CH_2NH(C_6H_5).COOC_2H_5)_2$.—This compound was prepared from diphenylethylenediamine by the two-phase method. The yield was practically quantitative. Recrystallized from alcohol or benzene, it formed needles; m. p., 88°.

Anal. Calcd. for $C_{20}H_{24}N_2O_4$: N, 7.87. Found: 7.85, 7.92.

Carbo-*n*-butoxy-ethyl-iso-urea, $HN:C(OC_2H_5).NH.COOC_4H_9$ (*o*-ethylallophanic butyl ester).—This was prepared from ethyl-iso-urea hydrochloride, potassium hydroxide and chlorocarbonic *n*-butyl ester by the two-phase method. The reaction mixture was cooled in ice. The product was recrystallized from ligroin (b. p., 65–90°), and melted at 77°. The yield was quantitative.

Anal. Calcd. for $C_8H_{16}N_2O_3$: N, 14.91. Found: 14.74.

The compound is readily soluble in alcohol, ether, benzene and vegetable oils. It was prepared for the purpose of comparing its pharmacological action with that of the carbethoxy-ethyl-iso-urea, already studied by one of us.[3]

Pharmacological Part

A preliminary examination of the physiological action of acetylphenylurethan and its two isomers has been made. Acetylphenylurethane was administered to guinea pigs and rabbits by subcutaneous injection in olive oil solution. Two cc. of a 10% solution produced in a guinea pig of 570 g. weight a mild central depression, which was decidedly increased by the injection of 1 cc. more, half an hour after the first injection. There was marked respiratory depression and some salivation. A dose of 0.35 g. given to a guinea pig of about the same weight as the first produced incoördination and drowsiness in about seven minutes. Respiration became dyspnoeic and the pulse rapid and arrhythmic. In 30 minutes the animal was deeply narcotized, but reflexes were still present. There was some involuntary muscular movement. Recovery was complete by next morning.

In a rabbit weighing 1700 g. a dose of 1.2 g. produced only mild central depression, but the rectal temperature fell from 38° to 35.1° in a little over two hours.

No very definite physiological action was elicited by either phenylacetylurethan or *p*-acetylphenylurethan. Their solubilities in oil are much less than that of acetylphenylurethan.

Carbo-*n*-butoxy-ethyl-iso-urea given by subcutaneous injection in olive oil produced only slight physiological effect. After a dose of 0.4 g. per kilogram a rabbit showed only a small fall of temperature in one hour. An additional dose of 0.5 g. had little or no effect. The total fall of temperature observed was 1°, and there was a scarcely perceptible central depression. This result is in striking contrast to the effect of the corresponding carbethoxy compound. Since the physical properties of the

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[3] Basterfield, *J. Pharmacol.*, **20**, 451 (1923).

two compounds are very similar it would seem that the *n*-butyl radical on oxygen is deficient in some way in its relation to the lipoids of the nervous system.

Summary

The preparation of various substituted urethans and of 1,3-diphenyl-2-iminobarbituric acid is described.

A preliminary study of the physiological action of acetylphenylurethan is reported.

SASKATOON, CANADA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF COLORADO]

THE CONDENSATION OF MESITYL OXIDE WITH ALIPHATIC KETONES

BY JOHN B. EKELEY AND M. SCOTT CARPENTER[1]

RECEIVED MAY 24, 1926 PUBLISHED SEPTEMBER 4, 1926

Introduction

The simplest of the unsaturated cyclic ketones that can be prepared by the condensation of an aliphatic ketone is 1,3,3-trimethyl-cyclohexenone-5, or the well-known isophorone. Recently methylethyl ketone[2] and diethyl ketone[3] have been subjected to the action of condensing agents and the corresponding homologs of isophorone have been isolated. In the case of methylethyl ketone it was shown that four isomeric homologs of isophorone are theoretically possible, and two of them were isolated, 1,2,3,6-tetramethyl-3-ethyl-cyclohexenone-5 and 1,3-diethyl-3,4-dimethyl-cyclohexenone-5, which have been designated, respectively, as γ- and δ-homoisophorones, each with the empirical formula $C_{12}H_{20}O$. The structure of these compounds was proved by the same method originally used by Knoevenagel.[4] In the case of diethyl ketone the only homolog of isophorone theoretically possible, 1,3,3-triethyl-2,4,6-trimethyl-cyclohexenone-5, having the empirical formula $C_{15}H_{26}O$, was prepared.

Thus by condensing the saturated aliphatic ketones, unsaturated cyclic ketones are formed, bearing the type formula $C_nH_{2n-4}O$. As the homologous series is ascended, it is apparent that for a carbon increment of one in the initial ketone, the carbon increment in the final product is three; thus, acetone (C_3H_6O) $\longrightarrow$ $C_9H_{14}O$; methylethyl ketone (C_4H_8O) $\longrightarrow$ $C_{12}H_{20}O$; diethyl ketone ($C_5H_{10}O$) $\longrightarrow$ $C_{15}H_{26}O$.

Other members of this cyclic series should exist, containing an interme-

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[1] From a thesis submitted by M. Scott Carpenter to the Graduate Faculty of the University of Colorado in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Ekeley and Howe, THIS JOURNAL, 45, 1917 (1923).

[3] Ekeley and Carpenter, *ibid.*, 46, 446 (1924).

[4] Knoevenagel, *Ann.*, 289, 10 (1895); 299, 160 (1897).

diate number of carbon atoms, C_{10}, C_{11}, C_{13}, C_{14}, etc. It seemed desirable that this series should be filled out, and the present investigation had for its purpose the preparation of some of these intermediate members.

We have condensed mesityl oxide with the following ketones: methylethyl, methylpropyl, diethyl, methylbutyl and methyl*iso*butyl. In all cases except that of diethylketone four isomers are theoretically possible. Diethyl ketone should yield but two. In no case was it possible by fractional distillation to isolate more than one product.

All of the compounds prepared have the general characteristics of isophorone and appear to belong to an homologous series. They immediately decolorize bromine water and dilute permanganate solution, give wine-red to violet colorations with ferric chloride and, very strangely, possess similar boiling points. The molecular refractions of these compounds are quite high, as compared to the values calculated for the keto form. They readily form semicarbazones that are insoluble in water and that crystallize in small, glistening plates from absolute alcohol. The semicarbazones are hydrolyzed almost instantly by dilute mineral acids, but are fairly stable in the presence of dil. acetic acid and alkalies. These derivatives possess melting points quite close to one another.

Experimental Part

Reagents.—Sodium ethylate was chosen for the condensing agent because it gives purer products than acid reagents. When concd. sulfuric acid is used the products are nearly always contaminated with sulfonic acids which sometimes are difficult to eliminate, while hydrogen chloride has a tendency to form hydrogen-chloride addition products which nearly always cause a darkening of the oils with time, regardless of the care which has been taken to free the products from these impurities. The sodium ethylate was prepared according to the method of Claisen, described by Lassar-Cohn.[5] The mesityl oxide used was prepared by the method of Locquin.[6] The methylethyl ketone used was purchased from the Eastman Kodak Company's Organic Laboratory and all the others were prepared by Kahlbaum. All the ketones were of a high degree of purity and were redistilled before use until they boiled constant to 0.5°.

Method.—A mixture of one molecular proportion of the ketone and one of mesityl oxide was cooled by immersing the flask in chipped ice. To this solution was added gradually while constantly shaking the flask 0.5 molecular proportion of powdered sodium ethylate. The solution, now of a pasty consistency, had assumed a deep reddish-brown color. The contents of the flask were protected from the atmosphere by means of a calcium chloride tube and set aside at a temperature of about 5°.

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[5] Lassar-Cohn, "Arbeitsmethoden für Organisch-Chemische Laboratorien," pp. 492, 729 (1923).

[6] Locquin, *Ann. chim.*, 19, 32 (1923).

After about ten days an equal volume of water was added to the condensation mixture, whereupon a deep brown, oily layer floated on the surface of the aqueous alkaline layer. The oily layer was separated and washed repeatedly with water until the washings were clear and reacted neutral to litmus. The aqueous alkaline layer was neutralized with acetic acid, which caused the further separation of a small quantity of oil. This oil was extracted with ether, the ethereal solution washed with water and added to the main body of the oil. Anhydrous sodium sulfate was added to the ethereal solution which was then allowed to stand overnight.

The solution was filtered from sodium sulfate and the ether distilled on the water-bath. The residual oil was subjected to fractional distillation under diminished pressure until a product was obtained showing a constant refractive index. The yields were small on account of the many possibilities of condensation.

Many attempts were made to isolate more than one of the four expected isomers and to increase the yield of the condensation. The proportions of ketone, mesityl oxide and condensing agent were altered over wide ranges; the duration of the condensation was lengthened to a month and shortened to a day; the temperature was varied from that of ice to that of a boiling water-bath; the reaction was carried out in the presence of sunlight and in the dark; sodium methylate, sodamide, barium hydroxide, diethylamine and piperidine were used in place of sodium ethylate. Trials were also made, using sodium in methyl and ethyl alcohol, in which the mixtures were immediately heated over a water-bath without preliminary standing in the cold. Yields much poorer than that given by the original procedure were obtained in many cases, but none better, and in no case was more than one product isolated. A certain amount of ketone seems doomed to be transformed into a thick, tarry mass, and a corresponding quantity of the ketone is recovered as such and as a polymerized condensation product.

Preparation of the Semicarbazones.—Semicarbazide hydrochloride was dissolved in the minimum quantity of water and sufficient sodium acetate added to neutralize the hydrochloric acid. An equimolecular quantity of the unsaturated ketone was added, and enough alcohol to form a clear solution. This solution was allowed to stand overnight at a temperature of 5–8°, at the end of which time an abundant crop of white crystals had separated. These were filtered from the mother liquor and washed repeatedly on the suction filter with cold 50% alcohol. Several recrystallizations from absolute alcohol yielded small glistening plates, insoluble in water, fairly soluble in alcohol and melting from 170° to 176° with decomposition beginning just before melting. The crystals were found to be hydrolyzed almost instantly by warm, dilute mineral acids, but were fairly stable in the presence of acetic acid and alkalies, and not noticeably affected by long contact with boiling water, in which they are quite insoluble.

Table I

Analyses

A. Condensation Products from Various Ketones

From ketone	Formula	Calcd. C, %	Calcd. H, %	Found C, %		Found H, %	
Methylethyl	$C_{10}H_{16}O$	78.88	10.59	78.67		10.25	
Methylpropyl	$C_{11}H_{18}O$	79.45	10.92	79.70	79.51	10.74	10.61
Diethyl	$C_{11}H_{18}O$	79.45	10.92	79.62	79.36	10.43	10.46
Methylbutyl	$C_{12}H_{20}O$	79.93	11.19	79.86	80.01	10.65	10.61
Methyl*iso*butyl	$C_{12}H_{20}O$	79.93	11.19	79.83	79.70	10.50	10.51

B. Semicarbazones

From ketone product	Formula	M. p., °C.	N, % Calcd.	N, % Found	
Methylethyl	$C_{11}H_{19}ON_3$	176	20.10	20.30	20.00
Methylpropyl	$C_{12}H_{21}ON_3$	172	18.83	18.62	18.87
Diethyl	$C_{12}H_{21}ON_3$	170	18.83	18.82	18.92
Methylbutyl	$C_{13}H_{23}ON_3$	172	17.71	17.53	17.83
Methyl*iso*butyl	$C_{13}H_{23}ON_3$	170	17.71	17.55	17.75

For comparative purposes, the physical constants of the unsaturated ketones are listed in Table II.

Table II

Physical Constants

Compound from	$CH_3COC_2H_5$ $C_{10}H_{16}O$	$CH_3COC_3H_7$ $C_{11}H_{18}O$	$(C_2H_5)_2CO$ $C_{11}H_{18}O$	$CH_3COC_4H_9$ $C_{12}H_{20}O$	$CH_3COCHCH(CH_3)_2$ $C_{12}H_{20}O$
B. p., °C.	99.5–100	122–126	102–105	119–121	101–104
Pressure, mm.	4.5	13	4	11	3
d_4^{20}	0.92811	0.92372	0.93062	0.92004	0.92616
n_D^{20}	1.5048	1.5112	1.5218	1.5130	1.5222
M_D	48.640	53.917	54.451	58.878	59.341
Exaltation from keto form	2.916	3.575	4.109	3.918	4.381

It will be noticed that the refractive indices and exaltations of all the compounds prepared from methyl ketones progress regularly as the series is ascended, while the diethyl compound presents an irregularity. The authors have no explanation to offer for the unusually high exaltations of the molecular refraction that have been observed. An exaltation is to be expected, since the first member of the series, isophorone, exhibits an exaltation of one unit, but an exaltation of more than four units as the series is ascended was entirely unlooked for.

Summary

1. Mesityl oxide has been condensed with the following ketones: methylethyl, methylpropyl, diethyl, methylbutyl and methyl*iso*butyl. In each case only one condensation product was isolated.
2. The semicarbazones of the unsaturated ketones have been prepared.

Boulder, Colorado

[Contribution from the Laboratories of the Rockefeller Institute for Medical Research]

THE PREPARATION OF URACIL FROM UREA

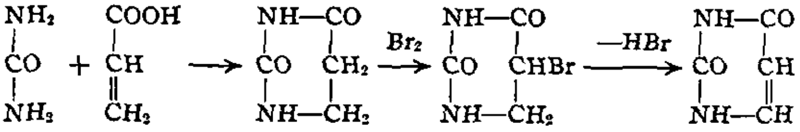
By David Davidson and Oskar Baudisch

Received May 27, 1926 Published September 4, 1926

Introduction

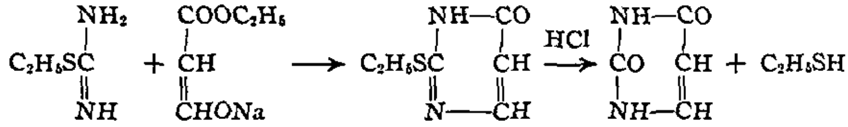
This paper deals with a convenient method of preparation of the pyrimidine uracil I directly from urea.

Uracil was isolated from the hydrolytic products of yeast nucleic acid by Ascoli[1] in 1900. Its wide distribution in plant and animal nucleic acids was demonstrated by the work of several investigators.[2] The discovery of uracil in nature was soon followed by its laboratory synthesis by Fischer and Roeder,[3] as illustrated below. A practical synthesis of uracil was then brought forward by Wheeler and Merriam,[4] which involved the following steps.



$$\begin{array}{c}NH_2\\|\\CO\\|\\NH_2\end{array} + \begin{array}{c}COOH\\|\\CH\\\|\\CH_2\end{array} \longrightarrow \begin{array}{cc}NH-&CO\\|&|\\CO&CH_2\\|&|\\NH-&CH_2\end{array} \xrightarrow{Br_2} \begin{array}{cc}NH-&CO\\|&|\\CO&CHBr\\|&|\\NH-&CH_2\end{array} \xrightarrow{-HBr} \begin{array}{cc}NH-&CO\\|&|\\CO&CH\\|&\|\\NH-&CH\end{array}$$

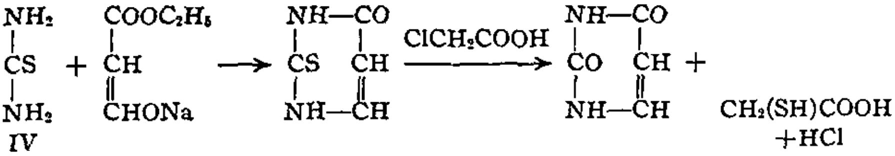
I



$$\begin{array}{c}NH_2\\|\\C_2H_5SC\\\|\\NH\end{array} + \begin{array}{c}COOC_2H_5\\|\\CH\\\|\\CHONa\end{array} \longrightarrow \begin{array}{cc}NH-&CO\\|&|\\C_2H_5SC&CH\\\|&\|\\N-&CH\end{array} \xrightarrow{HCl} \begin{array}{cc}NH-&CO\\|&|\\CO&CH\\|&\|\\NH-&CH\end{array} + C_2H_5SH$$

II III

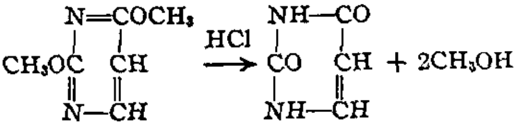
The substitution of thio-urea IV for ethyl pseudo-thio-urea II in this synthesis resulted in the excellent preparative method of Wheeler and Liddle.[5]



$$\begin{array}{c}NH_2\\|\\CS\\|\\NH_2\end{array} + \begin{array}{c}COOC_2H_5\\|\\CH\\\|\\CHONa\end{array} \longrightarrow \begin{array}{cc}NH-&CO\\|&|\\CS&CH\\|&\|\\NH-&CH\end{array} \xrightarrow{ClCH_2COOH} \begin{array}{cc}NH-&CO\\|&|\\CO&CH\\|&\|\\NH-&CH\end{array} + \begin{array}{c}CH_2(SH)COOH\\+HCl\end{array}$$

IV

Uracil has also been prepared by other workers; thus Gabriel and Colman obtained it by the hydrolysis of 2,4-dimethoxypyrimidine;[6]



$$\begin{array}{cc}N=&COCH_3\\|&|\\CH_3OC&CH\\\|&\|\\N-&CH\end{array} \xrightarrow{HCl} \begin{array}{cc}NH-&CO\\|&|\\CO&CH\\|&\|\\NH-&CH\end{array} + 2CH_3OH$$

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[1] Ascoli, *Z. physiol. Chem.*, **31**, 162 (1900).

[2] Osborne and Harris, *Z. physiol. Chem.*, **36**, 107 (1902). Kossel and Steudel, *ibid.*, **37**, 246 (1903). Levene, *ibid.*, **38**, 82 (1903); **39**, 6, 8 (1903). Levene and Stokey, *ibid.*, **41**, 404 (1904). Mandel and Levene, *J. Biol. Chem.*, **1**, 425 (1906). Osborne and Heyl, *Am. J. Physiol.*, **21**, 157 (1908). Levene and Jacobs, *Ber.*, **43**, 3133, 3161 (1910).

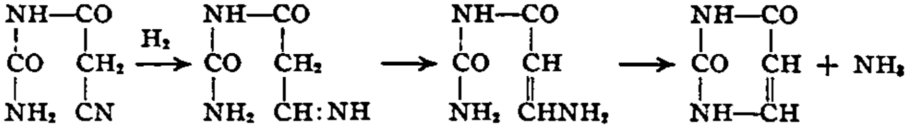
[3] Fischer and Roeder, *Ber.*, **34**, 3761 (1901).

[4] Wheeler and Merriam, *Am. Chem. J.*, **29**, 478 (1903).

[5] Wheeler and Liddle, *ibid.*, **40**, 547 (1908).

[6] Gabriel and Colman, *Ber.*, **36**, 3380 (1903).

while recently Rupe, Metzger and Vogler[7] have isolated it in the reduction of cyano-acetyl-urea.



$$\begin{array}{ll}\mathrm{NH}-&\mathrm{CO}\\ | & |\\ \mathrm{CO} & \mathrm{CH_2}\\ | & |\\ \mathrm{NH_2} & \mathrm{CN}\end{array} \xrightarrow{H_2} \begin{array}{ll}\mathrm{NH}-&\mathrm{CO}\\ | & |\\ \mathrm{CO} & \mathrm{CH_2}\\ | & |\\ \mathrm{NH_2} & \mathrm{CH{:}NH}\end{array} \longrightarrow \begin{array}{ll}\mathrm{NH}-&\mathrm{CO}\\ | & |\\ \mathrm{CO} & \mathrm{CH}\\ | & \|\\ \mathrm{NH_2} & \mathrm{CHNH_2}\end{array} \longrightarrow \begin{array}{ll}\mathrm{NH}-&\mathrm{CO}\\ | & |\\ \mathrm{CO} & \mathrm{CH}\\ | & \|\\ \mathrm{NH}-&\mathrm{CH}\end{array} + \mathrm{NH_3}$$

Previous Attempts to Synthesize Uracil from Urea

Aside from the synthesis of Fischer and Roeder which is *not* a satisfactory method of preparation[8] attempts have been made to prepare uracil directly from urea by Wheeler and Merriam[4] and by Wheeler and Liddle[5] who report unsuccessful efforts to condense urea with sodium formylacetic ester III in alkaline solution. Concerning the condensation in *acid* solution analogous to that used by Behrend[9] in the preparation of 6-methyluracil, Wheeler and Merriam state: "A method similar to that of preparing methyluracil by condensing urea with aceto-acetic ester by means of hydrochloric acid, has not been applied to the preparation of uracil, probably on account of the ease with which free formylacetic ester passes into trimesic ester." This presumption is confirmed by the experience of the present authors.[10]

[7] Rupe, Metzger and Vogler, *Helvetica Chim. Acta*, 8, 848 (1925).

[8] Fischer and Roeder, Ref. 3, p. 3761, state: "Bei dem keineswegs untergeordneten physiologischen Interesse, welches hiernach das Uracil besitzt, werden wir versuchen, die Synthese zu einer ausgiebigeren Darstellungsweise auszubilden, um eine genauere Untersuchung der Metamorphosen ausführen zu können."

[9] Behrend, *Ann.*, 229, 5 (1885).

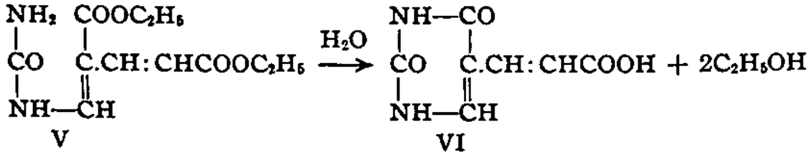
[10] When a solution of two moles of urea and the sodium formylacetic ester from 10 g. of sodium was treated with 150 cc. of concd. hydrochloric acid the solution became turbid and soon deposited a crystalline substance in fine needles. After two recrystallizations from alcohol it melted at 206–208°.

Anal. Calcd. for $C_{11}H_{16}O_5N_2$: C, 51.54; H, 6.30; N, 10.94. Found: C, 51.25; H, 6.34; N, 10.97, 10.83.

Its analysis indicates that it is a condensation product of one molecular proportion of urea with two of formylacetic ester. Its probable structure is that of ureidomethylene glutaconic ester V, and it presumably results from a reaction between urea and formylglutaconic ester which Wislicenus and others have shown to be formed by the acidification of sodium formylacetic ester. [Wislicenus and Bindemann, *Ann.*, 316, 20, 29 (1901). Wislicenus and von Wrangell, *Ann.*, 381, 367 (1911).] The product dissolved readily when heated with dilute alkali. Upon acidification crystals separated which decomposed at 285° and had the following composition.

Anal. Calcd. for $C_7H_6O_4N_2$: C, 46.15; H, 3.32; N, 15.39. Found: C, 46.27; H, 3.44; N, 15.25.

These analytical results indicate that the substance is uracil-5-β-acrylic acid VI resulting from the reaction

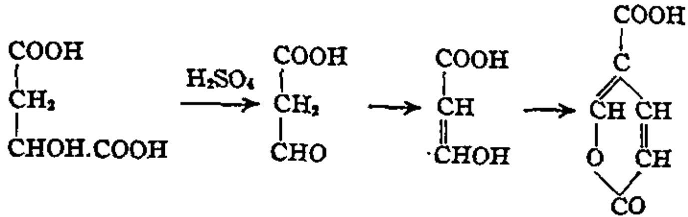


$$\begin{array}{ll}\mathrm{NH_2} & \mathrm{COOC_2H_5}\\ | & |\\ \mathrm{CO} & \mathrm{C.CH{:}CHCOOC_2H_5}\\ | & \|\\ \mathrm{NH}-&\mathrm{CH}\end{array} \xrightarrow{H_2O} \begin{array}{ll}\mathrm{NH}-&\mathrm{CO}\\ | & |\\ \mathrm{CO} & \mathrm{C.CH{:}CHCOOH}\\ | & \|\\ \mathrm{NH}-&\mathrm{CH}\end{array} + 2C_2H_5OH$$

V VI

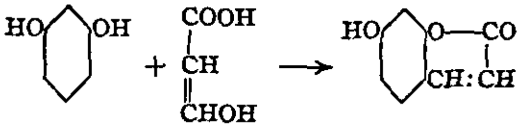
Discussion of the Synthesis

The synthesis dealt with in the present paper is based on a reaction discovered by von Pechmann.[11] Von Pechmann found that, on treatment

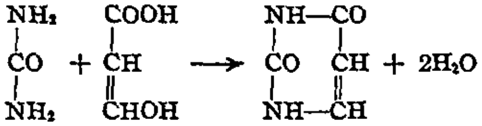


VII VIII IX X

with concd. sulfuric acid, malic acid VII split off formic acid (or CO + H_2O) yielding formylacetic acid (malonic semialdehyde) VIII. The latter product, however, immediately underwent autocondensation reacting in its enol form IX to give cumalinic acid X. Nevertheless, when a phenol was mixed with the malic acid the intermediate oxymethylene acetic acid reacted with the phenol and a coumarin resulted; thus, for example, with resorcinol[12]



It appeared to the authors that by treating a mixture of urea and malic acid with sulfuric acid a reaction might be obtained between urea and the transitory oxymethylene acetic acid.



$$\begin{array}{l}NH_2\\ |\\ CO\\ |\\ NH_2\end{array} + \begin{array}{l}COOH\\ |\\ CH\\ \|\\ CHOH\end{array} \longrightarrow \begin{array}{ll}NH—&CO\\ |&|\\ CO&CH\\ |&\|\\ NH—&CH\end{array} + 2H_2O$$

This expectation has been realized experimentally. By utilizing this reaction excellent yields of uracil of high degree of purity are readily obtainable in the course of several hours. The method eliminates the costly use of thio-urea and avoids the presence of objectionable traces of sulfur in the final product.[13]

The synthesis presented above affords a ready approach to many interesting products. Thus, by nitrating according to Johnson and Matsuo[14]

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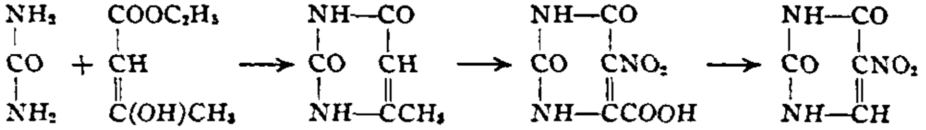
[11] (a) von Pechmann, *Ber.*, **17**, 936 (1884); (b) *Ann.*, **264**, 261 (1891).

[12] Ref. 11 a, p. 932.

[13] It is to be noted that the green color reaction of uracil with sodium aquo-pentacyano-ferroate described by Pfaltz and Baudisch [This Journal, **45**, 2973 (1923)] is not obtained with uracil prepared by the new method. Since, however, 2-thio-uracil gives a brilliant emerald-green color reaction with the complex iron salt, the reaction previously obtained is probably ascribable to the presence of sulfur-bearing impurities. The pyrimidines isolated from natural sources also give a green color with sodium aquo-pentacyano-ferroate and likewise are probably contaminated by sulfur compounds.

[14] Johnson and Matsuo, This Journal, **41**, 782 (1919).

5-nitro-uracil XI is obtained. This compound has previously been prepared from urea, but in three steps, utilizing aceto-acetic ester.[15]



XI

The new method in two steps, however, offers advantages in convenience and yields.

1,3-Dimethyluracil which has previously been prepared by the action of methyl iodide and potassium hydroxide or potassium uracil in alcoholic solution[16] is readily produced in excellent yield by methylating uracil in aqueous solution with sodium hydroxide and methyl sulfate.

Experimental Part

Preparation of Uracil.—Four hundred cc. of fuming sulfuric acid (15% of SO_3) is placed in a 2-liter round-bottomed flask and chilled to 0° in a freezing mixture. To it is gradually added during efficient mechanical stirring 100 g. of crystalline urea, the temperature being maintained below 10°. This step requires 15–20 minutes. One hundred g. of pulverized commercial malic acid is then added at once and the flask heated on the steam-bath for one hour. During the first 15 minutes large volumes of carbon monoxide are evolved which may be led away and burned. Carbon dioxide and sulfur dioxide are also produced during this operation, at the end of which the flask is cooled and its contents turned into 1200 cc. of water. On cooling, crude uracil separates. This is filtered off, washed with water (best by suspending in water and again filtering) and then recrystallized from 1250 cc. of boiling water with the aid of 10 g. of Darco charcoal. The product separates in snow-white needles which are dried at 100°; yield, 42–46 g., or 50–55%.

Anal. Calcd. for $C_4H_4O_2N_2$: C, 42.84; H, 3.60; N, 25.01. Found: C, 42.72; H, 3.69; N, 25.00.

Methylation of Uracil.—Twenty g. of uracil is dissolved in a solution of 17 g. of sodium hydroxide in 100 cc. of water. The solution is cooled in ice water while 40 cc. of methyl sulfate is gradually added during mechanical stirring. The mixture is then heated to boiling, cooled and extracted thrice with 100cc. portions of chloroform. The chloroform extract is filtered through a dry filter and evaporated, yielding 23.5 g. of 1,3-dimethyluracil melting at 123–124°; yield, 94%.

Anal. Calcd. for $C_6H_8O_2N_2$: N, 20.00. Found: 20.03.

The product may be recrystallized by dissolving in hot alcohol, cooling and adding an equal volume of ether.

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[15] Behrend and Roosen, *Ann.*, 251, 239 (1889). Biltz and Heyn, *Ann.*, 413, 110 (1916).

[16] Johnson and Clapp, *J. Biol. Chem.*, 5, 61 (1908).

Summary

An improved method for the synthesis of uracil is described.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

LECTURE EXPERIMENTS WITH THE NEW HALOGENOID, AZIDO-CARBONDISULFIDE

BY A. W. BROWNE AND R. S. VON HAZMBURG

RECEIVED JUNE 7, 1926 PUBLISHED SEPTEMBER 4, 1926

The surprising reactivity of azido-carbondisulfide toward various groups of substances, including acids, alkalies, oxidizing and reducing agents, and its susceptibility to autocatalytic decomposition even at ordinary temperatures, render available a series of instructive experiments suitable for use in lecture-table demonstration. Azido-carbondisulfide, itself a halogenoid, may be considered to contain potentially within its molecular structure three other halogenoids: $(SCN)_2$, $(CN)_2$ and $(N_3)_2$. Of these, thiocyanogen is evolved in the free state during thermal decomposition of the mother substance.

The experiments described in the present article are fairly representative of the large number that have been performed repeatedly by the authors at this University and elsewhere.

1. Demonstration of the Halogenoid Character of Azido-carbondisulfide.—(a) Like the halogens, azido-carbondisulfide reacts with aqueous solutions of potassium, sodium or ammonium hydroxide, yielding salts of the oxy-acid and hydracid corresponding, for example, to hypochlorous and hydrochloric acids. By acidification of the resulting solution, a reprecipitation of the white, crystalline halogenoid is effected.

Drop 0.5 g. of freshly prepared,[1] slightly moist azido-carbondisulfide into 100 cc. of approximately 1 *N* sodium hydroxide solution, either in a large test-tube or small cylinder, at ordinary or, better, at somewhat lower temperature. Acidify the yellow-green solution by gradual addition of 25–50 cc. of dilute (approximately 6 *N*) sulfuric acid. The precipitate may be identified by testing its behavior toward heat as outlined under Section 3.

(b) Despite its very limited solubility in water, azido-carbondisulfide is capable of discharging the iodide ion in aqueous solution to an appreciable extent, although the reaction normally proceeds in the opposite direction, as illustrated in the current method of preparing the halogenoid. In any case the equilibrium concentration of free iodine is sufficiently high to enable its detection by the usual test.

Introduce 0.5 g. of solid azido-carbondisulfide into 1 liter of a 1% aqueous

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[1] Browne, Hoel, Smith and Swezey, THIS JOURNAL, 45, 2541 (1923).

solution of potassium iodide containing 5 cc. of the usual starch solution. The characteristic deep blue coloration appears after the solution has been stirred for a few moments.

(c) The $SCSN_3^-$ ion reacts instantaneously, in aqueous solution, with the silver ion, forming the explosive, white precipitate, $AgSCSN_3$. Add to 1 liter of water 5 cc. of the concentrated solution of potassium (or sodium) azido-dithiocarbonate used in preparing the halogenoid under investigation. Introduce, drop by drop, a 10% solution of silver nitrate until precipitation is complete. The precipitate should never be filtered off or dried without suitable precautions for the protection of the operator from possible explosion.

2. Demonstration of the Production of Free Thiocyanogen from Azido-carbondisulfide.—Paint upon an ordinary sheet of writing paper, with the aid of a small camel's-hair brush, any desired word or pattern, using a 10% solution of azido-carbondisulfide in acetone. After the paper has dried, attach closely to it a second sheet, which has been previously impregnated with a 10% solution of ferric chloride and dried. When the first sheet of paper is gently warmed by rapidly and repeatedly passing the Bunsen flame over it, the pattern quickly develops as a result of a transformation of the invisible film of azido-carbondisulfide into the dark orange, polymeric thiocyanogen. The ferric chloride paper shows a similar pattern, in the deep red color of ferric thiocyanate, indicating the liberation of thiocyanogen, $(SCN)_2$, in the form of vapor.

3. Demonstration of the Instability of Azido-carbondisulfide.—The new halogenoid undergoes explosive decomposition when subjected (a) to mechanical impact, (b) to heat or (c) to the chemical action of a current of such gases as ammonia, hydrogen chloride or chlorine. The intensity of the explosion may vary from that of a mere puff, in case the sample is appreciably moist, to that of a sharp detonation, if it has been thoroughly dried. The importance of exercising extreme care in the preparation and use of azido-carbondisulfide or its compounds should be borne in mind at all times. It is inadvisable to store the dry halogenoid, even for a brief period, in any apparatus of glass or other material that might undergo fragmentation in the event of an explosion. The approved procedure is to keep the material between two pieces of filter paper, and to remove small samples for use with the aid of a bone spatula.

(a) Place a small sample (0.01 to 0.02 g.) of the halogenoid upon the polished surface of an iron plate or block, and strike it a sharp blow with a hammer.

(b) Heat a sample (0.02 to 0.2 g.) upon a piece of sheet iron with the aid of a Bunsen flame, or let the sample fall upon a metallic plate previously heated to 100° or higher.

Drop a sample (0.05 to 0.5 g.) into an iron water-bath containing water heated to from 80° to 100°. By means of a series of experiments at different temperatures within this range, the influence of temperature in accelerating the velocity of decomposition of the halogenoid may be strikingly demonstrated. In every case the sample may be observed to undergo incipient fusion and partial decomposition with evolution of gas before it explodes. The explosion usually consists of little more than a crackling or sputtering sound. The interval elapsing between the time of contact with the hot water and the time of explosion varies from about 10 to 12 seconds at 80°, to 4 to 6 at 85°, 2 to 3 at 90°, 1.5 to 2.5 at 95° and 1.0 to 1.5 at 100°.

(c) Arrange four portions of azido-carbondisulfide weighing approximately 0.02, 0.05, 0.15 and 0.4 g. about 10 cm. apart in a straight line on a wooden board. Direct a gentle stream of ammonia gas upon the samples in rapid succession, preferably beginning with the smallest. A series of explosions of increasing intensity will ensue.

Summary

The present article contains a brief description of several lecture experiments upon azido-carbondisulfide, $(SCSN_3)_2$, which serve to demonstrate (1) its halogenoid character, on the basis of its reaction with (a) sodium hydroxide, (b) potassium iodide and (c) silver nitrate; (2) its thermal decomposition, with formation of free thiocyanogen; (3) its sensitivity to (a) mechanical impact, (b) heat and (c) the chemical action of ammonia gas.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

OMEGA-CYCLOHEXYL DERIVATIVES OF VARIOUS NORMAL ALIPHATIC ACIDS. IV

BY G. S. HIERS[1] WITH ROGER ADAMS

RECEIVED JUNE 7, 1926 PUBLISHED SEPTEMBER 4, 1926

In a recent paper[2d] it was pointed out that the cyclic structure present in chaulmoogric and hydnocarpic acids was, among others, an important factor in the bactericidal effect of these acids on *B. leprae*. As a consequence other acids containing a cyclic structure in the omega position have been studied. The κ-cyclohexyl-undecanoic acid and the μ-cyclohexyltridecanoic acid were described in a previous paper.[2d] This investigation

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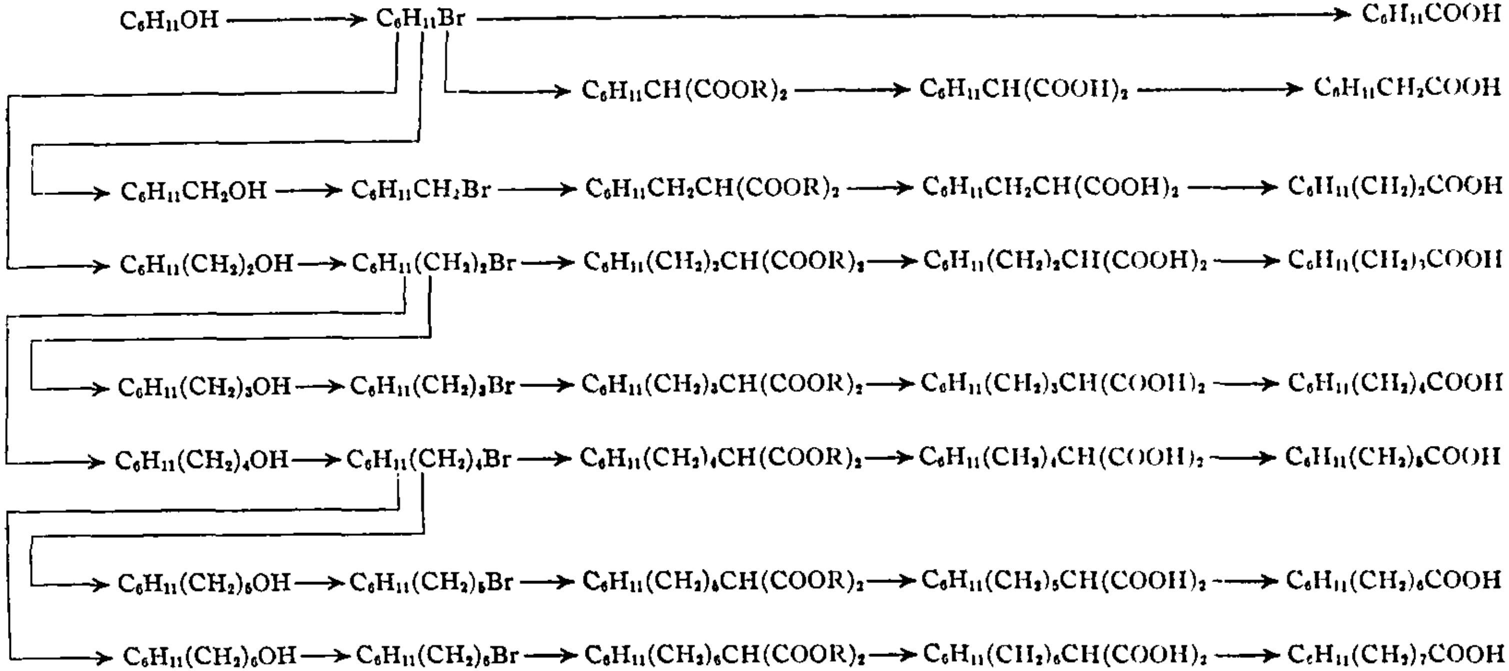
[1] This communication is an abstract of a portion of a thesis submitted by G. S. Hiers in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] For previous papers in this field see (a) Shriner with Adams, THIS JOURNAL, 47, 2727 (1925). (b) Noller with Adams, *ibid.*, 48, 1074; (c) 1080 (1926). (d) Hiers with Adams, *ibid.*, 48, 1089 (1926).

Table I

Preparation of ω-Cyclohexyl Acids



describes the completion of the synthesis of all of the ω-cyclohexyl acids containing from 1 to 13 carbon atoms in the side chain.

The hexahydrobenzoic acid was prepared merely by the action of carbon dioxide on the Grignard reagent from cyclohexyl bromide. All the other acids containing from two to eight carbon atoms inclusive in the side chain were made by the malonic ester synthesis from the proper bromide; the bromides were in turn prepared from the corresponding alcohols. Cyclohexyl bromide was converted into the Grignard reagent and treated either with formaldehyde to give cyclohexyl-carbinol or with ethylene oxide to give β-cyclohexyl-ethanol. These alcohols were then converted into their bromides and condensed with malonic ester to give the 3- and 4-carbon side-chain acids. The β-cyclohexylethyl bromide was converted to the Grignard reagent and with formaldehyde or ethylene oxide yielded γ-cyclohexyl-propanol or δ-cyclohexyl-butanol, respectively; by conversion to the bromides and condensation with malonic ester, the 5- and 6-carbon side-chain acids were obtained. By a similar procedure δ-cyclohexylbutyl bromide was converted to ε-cyclohexylpentyl bromide and ζ-cyclohexylhexyl bromide and these to the 7- and 8-carbon side-chain acids. These reactions are summarized in Table I.

The acids with side chains having more than 8 carbon atoms were prepared by the condensation of the proper Grignard reagent with the aldehyde esters obtained by the ozonation of methyl oleate, methyl undecylenate or methyl erucate.[2b] The 9-carbon side-chain acid was obtained from cyclohexyl bromide and methyl η-aldehydo-octanoate, the 10-carbon side-chain acid from cyclohexyl bromide and methyl θ-aldehydo-nonanoate, the 11-carbon side-chain acid from β-cyclohexylethyl bromide and methyl η-aldehydo-octanoate, the 12-carbon side-chain acid from β-cyclohexylethyl bromide and methyl θ-aldehydo-nonanoate and finally the 13-carbon side-chain acid from cyclohexyl bromide and methyl λ-aldehydo-dodecanoate. The hydroxy esters thus produced were changed to the oxygen free acids by conversion of the hydroxy esters into the bromides, then to the unsaturated acids and finally to the saturated acids.

The bacteriological results will be reported in detail elsewhere. It is sufficient to mention here that β-cyclohexyl-propionic acid which has a 3-carbon side-chain did show a slight action against the *B. leprae* and other acid-fast bacteria, killing in a concentration of 1:1000. With increase in length of side chain the substances rapidly became more effective until a maximum was reached in the 9-carbon side chain and then again diminished in effectiveness until it appeared only slight in the 13-carbon side-chain acid. The hydroxy acids containing 12- and 13-carbon side chains were far more effective than the corresponding acids without the hydroxyl group. The malonic acid derivatives showed almost no action. These tests were kindly made by Mr. G. H. Coleman.

Experimental Part

Preparation of Alcohols by the Use of a Grignard Reagent and Formaldehyde.—By the reaction of the proper Grignard reagent and formaldehyde, cyclohexyl-methanol,[3] γ-cyclohexyl-propanol[4] and ε-cyclohexyl-pentanol were prepared; the amounts of the bromides for each run employed in the syntheses were 163 g. of cyclohexyl bromide, 105 g. of β-cyclohexylethyl bromide and 81.5 g. of δ-cyclohexylbutyl bromide, with the proper amounts of other reagents. The yields were 71–76, 79 and 58%, respectively.

The reaction was carried out by leading the formaldehyde under the surface of the Grignard solution which was efficiently stirred while the reaction was taking place. The formaldehyde was prepared from paraformaldehyde which had been previously dried for three days over phosphorus pentoxide. The dry paraformaldehyde was heated to 160–180° for about two hours in a round-bottomed flask carrying a delivery tube to the reaction mixture. The amount of paraformaldehyde used was about twice the calculated quantity and the excess that entered the reaction mixture did no harm. The reaction product was refluxed for an hour longer. The product was carefully decomposed in the usual way with 30% sulfuric acid and ice.

Preparation of Alcohols by the Use of a Grignard Reagent and Ethylene Oxide.—By the condensation of the proper Grignard reagent and ethylene oxide, β-cyclohexyl-ethanol,[2d] δ-cyclohexyl-butanol and ζ-cyclohexyl-hexanol were prepared; the amounts of bromide employed in individual runs were 489 g. of cyclohexyl bromide, 191 g. of β-cyclohexylethyl bromide and 43.8 g. of δ-cyclohexyl bromide, respectively, and the yields of product amounted to 52, 47–53 and 37%.

The procedure[2d] has been described in detail in a previous paper. The maximum yield was obtained when the temperature of rearrangement was 60–65°. In general, after the initial reaction had been run, the ether was distilled and benzene was added at such a rate as to keep the volume constant until the temperature of rearrangement was reached. Then the reaction mixture was refluxed for one to two hours.

Preparation of the Cyclohexyl Alkyl Bromides.—The formation of the bromides from the alcohols was best carried out either with hydrobromic acid and sulfuric acid or with phosphorus tribromide. The former was more suitable for β-cyclohexylethyl bromide[2d] and γ-cyclohexylpropyl bromide; in the latter preparation 48 g. of γ-cyclohexyl-propanol was used in individual runs with yields of 77% of product. On the other hand, the phosphorus tribromide method gave better yields in the preparation

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[3] Noller and Adams, "Organic Syntheses," J. Wiley and Sons, New York, 1926, vol. 6, p. 22.

[4] Skita, *Ber.*, 48, 1688 (1915).

of cyclohexyl bromide[5] (300g. runs of cyclohexanol with yields of 75–77% of product), cyclohexylmethyl bromide[6] (40g. runs of cyclohexyl-methanol with yields of 60% of product), δ-cyclohexylbutyl bromide, (78g. runs of δ-cyclohexyl-butanol with yields of 74% of product), ε-cyclohexylpentyl bromide (33g. runs of ε-cyclohexyl-pentanol with yields of 74% of product) and ζ-cyclohexylhexyl bromide (13.5g. runs of ζ-cyclohexyl-hexanol with yields of 83% of product).

TABLE II

CYCLOHEXYL SUBSTITUTED ALCOHOLS

Formula	Physical constants B. p., °C.	n^{25}_D	d^{25}_4	Analysis Carbon, % Calcd.	 Found	 Hydrogen, % Calcd.	 Found
$C_6H_{11}OH$[7]	67– 68 (23 mm.)	1.4642	0.9441				
$C_6H_{11}CH_2OH$[8]	88– 89 (22 mm.)	1.4640	.9215				
$C_6H_{11}(CH_2)_2OH$[9]	87– 89 (6 mm.)	1.4636	.9183				
$C_6H_{11}(CH_2)_3OH$[4]	91– 92 (5 mm.)	1.4624	.9061	75.98	75.73	12.77	12.70
$C_6H_{11}(CH_2)_4OH$	103–104 (4 mm.)	1.4632	.9015	76.85	76.62	12.91	12.89
$C_6H_{11}(CH_2)_5OH$	118–119 (4 mm.)	1.4638	.8959	77.56	77.34	13.03	12.98
$C_6H_{11}(CH_2)_6OH$	123–124 (4 mm.)	1.4648	.8963	78.18	77.97	13.13	13.00

The hydrobromic acid-sulfuric acid method was essentially that described by Kamm and Marvel[10] except that 40% hydrobromic acid was used.

The phosphorus tribromide method consisted in cooling the alcohol to —5° and then adding slowly during stirring, so that the temperature did not rise above 0°, 20% excess over one-third of one molecular equivalent of

TABLE III

ω-CYCLOHEXYL SUBSTITUTED ALKYL HALIDES

Formula	Physical constants B. p., °C.	n^{25}_D	d^{25}_4	Analysis for Br, % Calcd.	 Found
$C_6H_{11}Br$[5a,b,10]	69–71 (30 mm.)	1.4917	1.3128		
$C_6H_{11}CH_2I$[6]	106–108 (26 mm.)	1.4922	1.3751		
$C_6H_{11}CH_2Br$[6]	76–77 (26 mm.)	1.4889	1.2690	45.15	44.78
$C_6H_{11}(CH_2)_2Br$	70.5–71 (6 mm.)	1.4862	1.2096	41.83	41.58
$C_6H_{11}(CH_2)_3Br$	77–79 (4 mm.)	1.4848	1.1521	39.17	38.92
$C_6H_{11}(CH_2)_4Br$	91.6–92.2 (4 mm.)	1.4832	1.1350	36.65	36.24
$C_6H_{11}(CH_2)_5Br$	113–114 (5 mm.)	1.4814	1.1198	34.44	34.03
$C_6H_{11}(CH_2)_6Br$	124–125 (4 mm.)	1.4802	1.1073	32.47	32.25

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[5] (a) Freundler and Damond, *Compt. rend.*, **141**, 594 (1905). (b) Kohler and Burnley, *Am. Chem. J.*, **43**, 413 (1910).

[6] (a) Freundler, *Compt. rend.*, **142**, 344 (1906). (b) *Bull. soc. chim.*, [3] **35**, 544 (1906).

[7] (a) Frydlender, *Rev. prod. chim.*, **23**, 719 (1920). (b) Skrauth, *Z. angew. Chem.*, **35**, 25 (1922).

[8] Sabatier and Mailhe, *Compt. rend.*, **139**, 344 (1904).

[9] Zelinsky, *Ber.*, **41**, 2628 (1908).

[10] Kamm and Marvel, "Organic Syntheses, J. Wiley and Sons, New York, **1921**, vol. 1, p. 1.

pure phosphorus tribromide. The mixture was stirred at room temperature for two hours, then at 100° for one hour. Upon cooling, the product was extracted thrice with low-boiling petroleum ether, this extract washed with water, dried with calcium chloride and then washed once with a little cold, concd. sulfuric acid, dried again and distilled under diminished pressure.

Hexahydrobenzoic Acid.—This was prepared by the general procedure described by Gilman[11] from 571 g. of cyclohexyl bromide, 85 g. of magnesium and 1 liter of ether. There was obtained on the average 309–313 g. (69–70%) of hexahydrobenzoic acid.

Cyclohexyl Alkyl Malonic Esters.—The condensation of the cyclohexyl alkyl bromides with malonic ester was carried out in the usual way, taking particular care to have a high grade of absolute alcohol and to distil on a steam-bath, after the reaction had taken place, as much alcohol as possible before diluting the reaction mixture with water. It was generally desirable finally to extract the ester with a little ether as it did not always separate well from the aqueous suspension.

Cyclohexyl Alkyl Malonic Acids.[12]—These were prepared by adding the ester slowly during stirring to a hot 50% potassium hydroxide solution. The mixtures were then heated for eight hours on a steam-bath to distil all of the alcohol produced by saponification, then cooled and acidified with hydrochloric acid using Congo red paper as an indicator. During neutralization, the temperature was kept below 20°. The malonic acids were extracted with ether, the ether was evaporated and the products were purified from benzene.

TABLE IV

ω-CYCLOHEXYL SUBSTITUTED MALONIC ESTERS

Formula ($R = CO_2C_2H_5$)	Preparation Bromide used, g.	Preparation Yield of ester, %	Physical constants B. p., °C.	Physical constants n_D^{25}	Physical constants d_4^{25}	Analysis Carbon, % Calcd.	Analysis Carbon, % Found	Analysis Hydrogen, % Calcd.	Analysis Hydrogen, % Found
$C_6H_{11}CH(R_2)$[a]	62	44	122–123 (4 mm.)	1 4478	1 0228				
$C_6H_{11}CH_2CH(R_2)$[b]	24	71	135–136 (3 mm.)	1.4469	1 0059	65.58	65 32	9 44	9 51
$C_6H_{11}(CH_2)_2CH$-(R_2)	32	50	139.8–140.2 (3 mm.)	1.4476	0.9956	66.61	66 53	9 70	9.69
$C_6H_{11}(CH_2)_3CH$-(R_2)	42	53	153.5–154 (4 mm)	1.4489	9870	67.55	67.35	9 93	10.04
$C_6H_{11}(CH_2)_4CH$-(R_2)	22	85	169–170 (5 mm.)	1.4500	9787	68.40	68 18	10 14	9 98
$C_6H_{11}(CH_2)_5CH$-(R_2)	30	79	186–187 (6 mm.)	1.4509	.9717	69 17	69.06	10.33	10.28
$C_6H_{11}(CH_2)_6CH$-(R_2)	26	63	192–193 (4 mm.)	1 4522	.9647	69 88	69 69	10.50	10 40

[a] Ref. 6 a.

[b] Ref. 10.

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[11] Gilman and Parker, "Organic Syntheses," J. Wiley and Sons, New York, 1925, vol. 5, p. 75.

[12] (a) Hope and Perkin, *J. Chem. Soc.*, 95, 1363 (1909). (b) Sabatier and Murat, *Compt. rend.*, 156, 426 (1913). Ref. 6. (c) J. Gutt, *Ber.*, 40, 2067 (1907).

Decomposition of Cyclohexyl Alkyl Malonic Acids to Monobasic Acids.[13]—The malonic acids were heated in a small, round-bottomed flask at a temperature 20–30° above the melting point for two to three hours. The resulting acids were then distilled under diminished pressure. The yields are based on distilled product.

TABLE V

CYCLOHEXYL SUBSTITUTED MALONIC ACIDS

Formula	Yield, %	Physical constants M. p., °C.	Neut. equiv., found	Mol. wt., calcd.	Analysis Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found
$C_6H_{11}CH(CO_2H)_2$[a]	97	183–184	186.4	186.11				
$C_6H_{11}CH_2CH(CO_2H)_2$[b]	95	114–115	200.9	200.13	59.96	59.62	8.06	7.86
$C_6H_{11}(CH_2)_2CH(CO_2H)_2$	84	129–130	214.2	214.14	61.64	61.24	8.47	8.22
$C_6H_{11}(CH_2)_3CH(CO_2H)_2$	92	88–89	229.8	228.16	63.11	62.89	8.83	8.70
$C_6H_{11}(CH_2)_4CH(CO_2H)_2$	97	118–119	242.6	242.18	64.42	64.19	9.15	9.07
$C_6H_{11}(CH_2)_5CH(CO_2H)_2$	93	111–112	257.7	256.19	65.58	65.31	9.44	9.22
$C_6H_{11}(CH_2)_6CH(CO_2H)_2$	94	114–115	271.0	270.21	66.61	66.27	9.70	9.61

[a] Melting point reported as 176–178°. See Ref. 12a.

[b] Melting point reported as 106.5°. See Ref. 13.

The Formation of Cyclohexyl Substituted Acids by the Condensation of the Proper Grignard Reagent with Various Aldehyde Esters.[14]—The general procedure for such condensations has been described in a previous paper.[2d]

θ-Cyclohexyl-θ-hydroxy-nonanoic Acid, θ-Cyclohexyl-nonanoic Acid.—From 80 g. of methyl η-aldehydo-octanoate[2b] and cyclohexylmagnesium bromide there was obtained after three fractional distillations 25 g. (23%) of methyl *θ-cyclohexyl-θ-hydroxy-nonanoate*; b. p., 186–192° at 5 mm. This was converted into the hydroxy acid by boiling with aqueous alcoholic potassium hydroxide. The hydroxy ester was converted into θ-cyclohexyl-nonanoic acid through the bromide and olefinic acid. No attempt was made to purify completely these last two intermediates. The final acid was purified by crystallization from 80% alcohol.

ι-Cyclohexyl-ι-hydroxy-decanoic Acid, ι-Cyclohexyldecanoic Acid.—From 48 g. of methyl θ-aldehydo-nonanoate[2b] and cyclohexylmagnesium bromide there was obtained after four fractional distillations 15.4 g. (23%) of methyl ι-cyclohexyl-ι-hydroxy-decanoate; b. p., 191–195° at

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[13] Zelinsky, *Ber.*, **41**, 2676 (1908).

[14] (a) Sabatier and Murat, *Compt. rend.*, **156**, 752 (1913). (b) Fokin and Willstätter, *Rec. trav. chim.*, **35**, 261, 285 (1916). (c) Ipatiew, *Ber.*, **42**, 2098 (1909).

4 mm. This was saponified and the corresponding hydroxy acid crystallized from acetone. The hydroxy ester was converted into ι-cyclohexyldecanoic acid which was purified from 70% alcohol and then from low-boiling petroleum ether.

λ-Cyclohexyl-ι-hydroxy-dodecanoic Acid, λ-Cyclohexyl-dodecanoic Acid.—From 47 g. of methyl θ-aldehydo-nonanoate[2b] and β-cyclohexylethylmagnesium bromide there was obtained after three fractional distillations 10 g. (14%) of methyl λ-cyclohexyl-ι-hydroxy-dodecanoate, b. p., 214–218° at 4 mm. The corresponding hydroxy acid proved to be difficult to purify. The hydroxy ester was converted into λ-cyclohexyl-dodecanoic acid which was crystallized from 75% alcohol, then from petroleum ether.

TABLE VI

ω-CYCLOHEXYL SUBSTITUTED HYDROXY FATTY ACIDS

Formula	Physical constants			Analysis			
				Carbon, %		Hydrogen, %	
	M p., ° C.	Neut. equiv., found	Mol wt. calcd.	Calcd.	Found	Calcd.	Found
$C_6H_{11}CHOH(CH_2)_7CO_2H$	78–79	254 2	256.22	70.25	69 97	11.02	10.94
$C_6H_{11}CHOH(CH_2)_8CO_2H$	63–64	267.2	270.24	71.05	70.84	11.19	11.23
$C_6H_{11}(CH_2)_2CHOH(CH_2)_7CO_2H$	75–76[2d]						
$C_6H_{11}(CH_2)_2CHOH(CH_2)_8CO_2H$[a]	58–59	291.1	298 27				
$C_6H_{11}CHOH(CH_2)_{11}CO_2H$	72–73[2d]						

[a] The substance was difficult to purify and was, therefore, converted directly into the hydroxyl free acid.

TABLE VII

ω-CYCLOHEXYL SUBSTITUTED FATTY ACIDS

Acid[a] R(R')nCOOH[a]	Yield, %	B. p., °C 4 mm.	M p., °C,	n_D^{18} 1.—	d_4^{20}	Neut. equiv. found	Mol. wt. calcd.	Analyses			
								C., %		H., %	
								Calcd.	Found	Calcd.	Found
R[b]	70	105–6	29–30	4520	1.0251	128 3	128.1				
RR'[c]	88	116–7	29–30	4537	1 0020	141 5	142.1				
RR'_2[d]	88	125–6	15–16	4553	0 9848	154.9	156 1				
RR'_3	85	132–4[e]	29–30	4562	.9693	169 8	170.1	70 53	70 45	10.67	10 63
RR'_4	82	151–3[f]	6–8	4570	9589	184 2	184 2	71 68	71 52	10 95	10 87
RR'_5	91	157–8	33–34	4580	.9506	196 5	198 2	72 66	72 58	11.19	11.13
RR'_6	93	171–2	25–26	4588	.9436	211.5	212.2	73 52	73 29	11 40	11.66
RR'_7	88	182–3	37–38	4598	9359	224.3	226.2	74.27	74 01	11 59	11.32
RR'_8	..	...	45 5–6.5	...	..	242 2	240.2	74 93	75 10	11.75	11 80
RR'_9	..	...	52.5–3.5	...	...	253.6	254 2	75.52	75 70	11.89	11.74
RR'_{10}	..	...	58–59	...	...	267.1	268.2	...	...	...	...
RR'_{11}	..	...	61.5–2	...	...	280.2	282 3	76.52	76 36	12 14	12 07
RR'_{12}	..	...	63–64	...	...	297.9	296.3	...	...	...	...

[a] $R = C_6H_{11}$; $R' = CH_2$.

[b] Refs. 15, 11.

[c] Refs. 6 a, 12 a, 12 c.

[d] Refs. 10, 14 a.

[e] 3 mm. pressure.

[f] 5 mm. pressure.

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[15] Godchat, *Bull. soc. chim.*, [4] 9, 261 (1911). Grignard and Billet, *Compt. rend.*, 155, 46 (1912).

Summary

1. A series of ω-cyclohexyl acids containing from 1 to 13 carbon atoms in the side chain have been prepared.

2. Those with from three to nine carbon atoms in the side chain show bactericidal action toward *B. leprae.*

3. A number of hydroxy-substituted acids of the above-mentioned series, formed as intermediates, also show bactericidal action.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

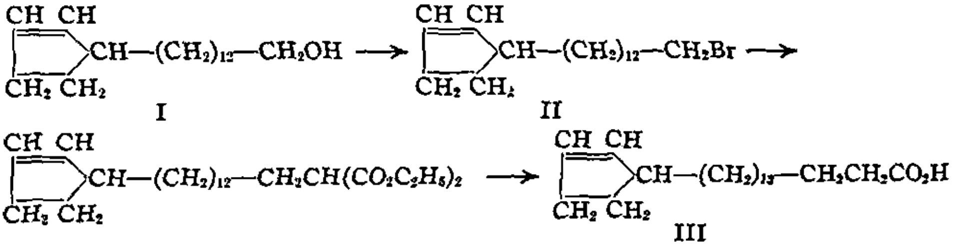
SYNTHESIS OF CHAULMOOGRYLACETIC ACID. V

BY RUSSEL H. VANDYKE[1] AND ROGER ADAMS

RECEIVED JUNE 7, 1926 PUBLISHED SEPTEMBER 4, 1926

Although it has been known for several years that hydnocarpic and chaulmoogric acids have a specific action against *B. leprae,* very few derivatives or compounds closely related to these two acids have been synthesized and studied. This paper describes the salts of chaulmoogryl acetic acid. Incidentally, the intermediates necessary for this synthesis are valuable for producing other compounds in which the chaulmoogryl nucleus is present.

The procedure was to esterify pure chaulmoogric acid to the ethyl ester. This latter compound was reduced to chaulmoogryl alcohol I by means of sodium and alcohol. The alcohol was converted to the bromide II and the bromide to chaulmoogrylacetic acid III by a malonic ester synthesis.



Experimental Part

Ethyl Chaulmoograte.—This was prepared according to the method of Power and Gornall.[2]

Chaulmoogryl Alcohol.—The reduction of ethyl chaulmoograte was attempted under a variety of conditions. The best yield was obtained by following the general procedure of Grün and Wirth.[3]

A 2-liter, round-bottom, 3-neck flask, fitted with a mechanical stirrer and long condenser was used. A solution of 70 g. of ethyl chaulmoograte in 230 cc. of absolute al-

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[1] This paper is an abstract of a portion of a thesis submitted by R. H. VanDyke in partial fulfilment of the requirements for the degree of Master of Arts in Chemistry at the University of Illinois.

[2] Power and Gornall, *J. Chem. Soc.*, **85**, 838 (1904).

[3] Grün and Wirth, *Ber.*, **55**, 2206 (1922).

cohol (100%) was placed in a flask, warmed and then 23 g. of freshly cut sodium added as rapidly as possible to the stirred solution. The stirring was continued until all of the sodium was dissolved. About 300 cc. of water was added and most of the alcohol distilled from a steam-bath. The mixture was extracted with ether. After washing and drying, the solvent was removed and the chaulmoogryl alcohol distilled. It boiled at 222° at 16 mm and melted at 36° (these constants agree with those of Power[3]). The yield was much better than obtained by Power, on the average 33 g (55%).

Anal. Subs., 0.8167, made up to 15 cc. in $CHCl_3$ gave a rotation of +3.18 in a 1-dcm. tube; $[\alpha]_D = +58.47°$.

Chaulmoogryl Bromide.—A solution of 10 g. of chaulmoogryl alcohol in 30 cc of dry toluene was placed in a small flask protected by a calcium chloride tube The flask was set in an ice-bath and to it was added carefully 7 g. of phosphorus tribromide dissolved in 10 cc. of toluene. This was allowed to stand at 0° for about three hours, after which it was heated on a steam-bath for three to five hours, or until no more hydrogen bromide was evolved. The reaction mixture was extracted with petroleum ether (40–50°), the ether extracted, washed with water and then with 10% sodium hydroxide solution. After drying, the mixture was distilled to remove the toluene and petroleum ether and the resulting bromide fractionated under diminished pressure It was a colorless oil boiling at 230° at 16 mm. and melting at 18 6°; n_D, 1.4846, d^{25}_{25}, 1.0461. The average yield was about 9 g. (70%).

Anal. Subs., 1.9890, made up to 15 cc. in $CHCl_3$ gave a rotation of 7.016 in a 1-dcm. tube; $[\alpha]_D = 52\ 92°$. Pure bromide in a 1-dcm. tube gave a rotation of 44.175°; $[\alpha]_D = 42.1°$

Subs., 0 2639, 0.2740; 8 02, 8 38 cc. of 0 09947 *N* $AgNO_3$. Calcd. for, $C_{18}H_{33}Br$; Br, 24.31. *Found*. 24 21, 24.35.

Chaulmoogrylmalonic Ester.—This was made by the usual procedure for condensing alkyl halides with malonic ester. The product was distilled under diminished pressure but no attempt was made to get a constant boiling point. The crude product was saponified directly.

Chaulmoogrylmalonic Acid.—A mixture of 5 g. of the crude chaulmoogrylmalonic ester was refluxed for four or five hours with 100 cc. of 10% potassium hydroxide solution The alkaline solution was diluted and extracted with ether to remove the unsaponified ester. It was then made acid with dil. hydrochloric acid, and the chaulmoogrylmalonic acid extracted with ether. It was purified by crystallizing from benzene. It formed small, white, needle-like crystals melting at 94–95°.

Anal. Subs , 0.5191, made up to 15 cc. in $CHCl_3$ in a 1-dcm. tube gave a rotation of +1.557°; $[\alpha]_D = +45.0°$.

Subs , 0.1150; 6.76 cc. of 0.09618 *N* NaOH. Calcd. for $C_{21}H_{36}O_4$: neut. equiv., 176. Found: 176.8.

Chaulmoogrylacetic Acid.—A solution of 2 g. of pure chaulmoogrylmalonic acid in 20 cc. of xylene was refluxed for two to three hours. On cooling, a white crystalline product separated in the xylene which, after a few crystallizations from 80% alcohol and petroleum ether, came to a constant melting point at 72–73°.

Anal. Subs., 0.6705, made up to 15 cc. in $CHCl_3$ in a 1-dcm. tube gave a rotation of 1.9376°; $[\alpha]_D = 43.34°$.

Subs., 0.2024: 6.53 cc. of 0.1008 N KOH. Subs., *0.1012:* CO_2, *0.2900;* H_2O, *0.1047.* Calcd. for $C_{20}H_{36}O_2$: neut. equiv., 308; C, 77.85; H, 11.77. Found: neut. equiv., 307.6; C, 78.1; H, 11.57.

Summary

Chaulmoogrylacetic acid has been prepared by converting ethyl chaulmoograte to chaulmoogryl alcohol, the alcohol to the bromide and finally by using a malonic ester synthesis on this last product.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

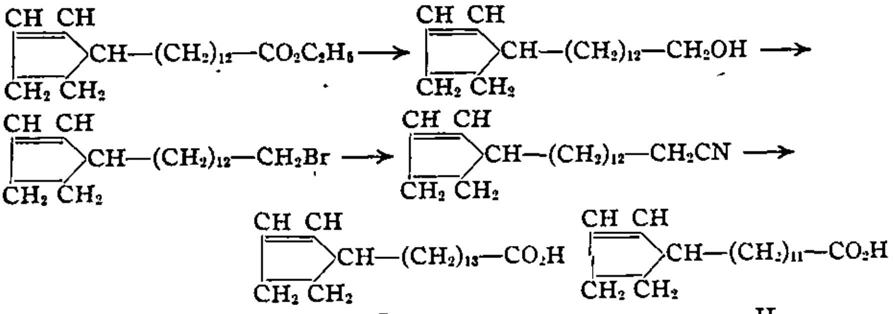
THE SYNTHESIS OF HOMOCHAULMOOGRIC ACID, HOMOHYDNOCARPIC ACID AND CHAULMOOGRYLAMINES. VI

BY J. SACKS[1] WITH ROGER ADAMS

RECEIVED JUNE 7, 1926 PUBLISHED SEPTEMBER 4, 1926

In continuation of the investigations[2] into the structure, synthesis and specificity[3] of the action of the fatty acids of chaulmoogra oil on *B. leprae*, a number of simple derivatives of chaulmoogric and hydnocarpic acids, the principal acids of chaulmoogra oil,[4] have been made and tested for their activity against certain acid-fast bacteria. A few other compounds containing a cyclic structure have also been tested. This report is a résumé of the chemical work and contains a brief statement of the bacteriological results. The detailed bacteriological results will be published elsewhere.

The homochaulmoogric acid I and homohydnocarpic acid II have been made from chaulmoogric acid and hydnocarpic acid, respectively, by the following general series of reactions, as illustrated by the formation of the homochaulmoogric acid:



I II

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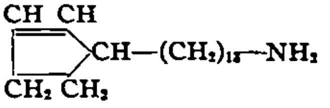
[1] This communication is an abstract of a portion of a thesis submitted by J. Sacks in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry in the Graduate School of the University of Illinois.

[2] (a) Shriner and Adams, THIS JOURNAL, 47, 2727 (1925). (b) Noller with Adams, *ibid.*, 48, 1074, 1080 (1926). (c) Hiers with Adams, *ibid.*, 48, 1089 (1926); 48, 2385 (1926). (d) VanDyke and Adams, *ibid.*, 48, 2393 (1926).

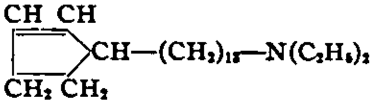
[3] Rogers, *Brit. Med. J.*, 1, 147 (1919); *Indian Med. Gaz.*, 54, 165 (1919); Walker and Sweeney, *J. Infectious Dis.*, 26, 238 (1925).

[4] (a) Power and Gornall, *J. Chem. Soc.*, 85, 838, 851 (1904). (b) Power and Barrowcliff, *ibid.*, 87, 884 (1905). (c) Barrowcliff and Power, *ibid.*, 91, 557 (1907).

In addition to these acids, chaulmoogrylamine III and chaulmoogryldiethylamine IV, respectively, were made by condensing chaulmoogryl bromide with potassium phthalimide and hydrolyzing the product, and by the condensation of the bromide with diethylamine.



III



IV

Besides these new synthetic derivatives just mentioned, the following substances were tested bacteriologically: cinnamic acid and its derivatives; *m*-nitro-, *m*-amino-, *p*-methoxy-cinnamic acids; *o*-coumaric acid and hydrocinnamic acid; the cyclopentane derivatives, Δ^1-cyclopentene-carboxylic acid, Δ^1-cyclopentenyl-acetic acid,[5a] and cyclopentanol-acetic acid;[5b] the cyclohexane derivatives, Δ^1-cyclohexene-carboxylic acid,[6] Δ^1-cyclohexenyl-acetic acid,[5] cyclohexanol-acetic acid[5] and cyclohexylidene-acetic acid;[5a] phenylpropiolic acid, cinnamylidene-acetic acid,[7] cinnamylidene-malonic acid,[8] furyl-acrylic acid and umbelliferone-β-acetic acid.

The hydnocarpic, homohydnocarpic, chaulmoogric, homochaulmoogric and chaulmoogrylacetic acids (the last was described by VanDyke and Adams[2d] in the preceding paper) present an interesting series for bacteriological testing since the difference in the individual compounds consists merely in the length of the side chain, varying from 11 to 15 carbon atoms. The tests have shown that the homo acids have very little effect. The chaulmoogrylacetic acid has practically no effect as compared with hydnocarpic and chaulmoogric acids.

Among the other compounds tested, cinnamic acid showed inhibitory power at a concentration of 1 : 1000, as has been previously demonstrated by Schöbl.[9] The cinnamic acid derivatives had no effect. Furyl-acrylic acid gave about the same results as cinnamic acid. Phenylpropiolic acid at a concentration of 1 : 1000 caused growth to be less rapid than in the controls. Cinnamylidene-acetic acid and umbelliferone-β-acetic acid showed rather marked inhibitory properties. The other compounds were without action.

Experimental Part

Chaulmoogric and Hydnocarpic Acids.—The procedure for obtaining these acids was a very slight modification of that used by Shriner.[2a] The mixed fatty acids, after being heated under diminished pressure to remove water, were distilled at 3–7 mm. pressure and separated into three portions, A, B and C, of which the middle one, B, was somewhat larger than the end

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[5] (a) Wallach, *Ann.*, **353**, 288 (1907); (b) **347**, 324 (1906).

[6] Aschan, *Ann.*, **271**, 265 (1893).

[7] Perkin, *J. Chem. Soc.*, **31**, 403 (1877).

[8] Stuart, *ibid.*, **49**, 365 (1886).

[9] Schöbl, *Phil. J. Sci.*, **23**, 533 (1923); **24**, 135 (1924).

portions. The low-boiling fraction, A, was worked up as follows. A fractional distillation of 600 g. was made at 3 mm. and four equal fractions were separated. The middle fractions were crystallized five times from two volumes of acetone, after which the product melted at 59–60°, the melting point of pure hydnocarpic acid. The yield was 33 g.

The high-boiling fraction, C, was crystallized once from 90% alcohol, twice from 80% alcohol and twice from ligroin, after which the melting point was 68–68.5°, the melting point of pure chaulmoogric acid. The yield was 400 g. from 8 kg. of oil.

Chaulmoogryl Cyanide.—A mixture of 15 g. of chaulmoogryl bromide[3] in 25 cc. of ethyl alcohol and 4 g. of potassium cyanide in 5 cc. of water was refluxed for 15 hours. Water was then added and the nitrile extracted with ether. After the ether solution had been dried, the solvent was removed and the nitrile distilled under diminished pressure. There was obtained 11 g. (87%) of a product boiling at 230° (16 mm.); m. p., 24.5°; n_D^{26}, 1.4691; d_{25}^{26}, 0.8928.

Anal. Subs., 0.9095 g., made up to 15 cc. in $CHCl_3$ gave a rotation of 3.00° in a 1-dcm. tube; $[\alpha]_D = 49.5°$.

Subs., 0.3912, 0.3182: 20.59, 15.48 cc. of 0.0714 *N* HCl. Calcd. for $C_{19}H_{33}N$: N, 5.09. Found: 5.03, 4.86.

Homochaulmoogric Acid, I.—A solution of 10 g. of chaulmoogryl cyanide in 50 cc. of alcohol was mixed with a solution of 1 g. of sodium hydroxide in 5 cc. of water. After refluxing for 16 hours, the solution was cooled, extracted once with ligroin, the free acid precipitated with hydrochloric acid and crystallized once from 80% alcohol and twice from ligroin. The pure substance was obtained in a yield of 6 g. and melted at 66–67°.

Anal. Subs., 0.5090, made up to 15 cc. in $CHCl_3$ gave a rotation of +1.84° in a 1-dcm. tube; $[\alpha]_D = +54.0°$.

Subs., 0.2513, 0.2613: 8.52, 8.83 cc. of 0.1 *N* NaOH. Calcd. for $C_{19}H_{34}O_2$: neut. equiv., 294.3. Found: 294.9, 295.9.

Chaulmoogrylamine Hydrochloride, III.—A mixture of 20 g. of chaulmoogryl bromide and 11.5 g. of potassium phthalimide was heated at 180° for 10 hours during mechanical agitation. After cooling, the reaction mixture was extracted with ether, the extract filtered and evaporated. The residue of crude chaulmoogryl-phthalimide was refluxed for 15 minutes with an excess of 10% potassium hydroxide solution, whereby it was converted to the potassium salt of the phthalamidic acid. The solution was then made strongly acid with hydrochloric acid and refluxed for 15 minutes to complete the hydrolysis. The acid solution was extracted with ether and then made alkaline. The chaulmoogrylamine was extracted with ether, the solution dried over solid potassium hydroxide, the solvent removed and the chaulmoogrylamine distilled under diminished pressure. The substance boiled at 206° (16 mm.). The yield was rather low, due possibly to the ease with which the amine absorbed carbon dioxide.

A solution of the amine in dry ether was treated with dry hydrogen chloride. The hydrochloride immediately separated. It was filtered and washed with ether. The chaulmoogrylamine hydrochloride was readily soluble in chloroform. It can be crystallized from hot water, and when pure melts at 114°.

Anal. Subs., 1.2655, made up to 15 cc. in $CHCl_3$ gave a rotation of +3.73° in a 1-dcm. tube; $[\alpha]_D = +44.2°$.

Subs., 0.2256, 0.2008: 14.82, 13.25 cc. of 0.05 *N* $AgNO_3$. Calcd. for $C_{18}H_{36}NCl$: Cl, 11.84. Found: 11.62, 11.71.

Chaulmoogryldiethylamine, IV.—A mixture of 10 g. of chaulmoogryl bromide with 9 g. of diethylamine was allowed to stand at room temperature for two days. Water was then added and the solution made alkaline with sodium hydroxide. The amine was taken up in ether, the ether washed well with water and dried over solid potassium hydroxide. After filtration, dry hydrogen chloride was passed into the solution and the solid hydrochloride separated. This was purified by dissolving in chloroform and precipitating with ligroin. It melts at 99°.

Anal. Subs., 1.103 g., made up to 15 cc. in $CHCl_3$ gave a rotation of +2.53° in a 1-dcm. tube; $[\alpha]_D = +34.5°$.

Subs., 0.1719, 0.1989: 10.03 cc., 11.37 cc. of 0.05 *N* $AgNO_3$. Calcd. for $C_{22}H_{44}NCl$: Cl, 9.92. Found: 10.10, 10.03.

Ethyl Hydnocarpate.—This was prepared by the procedure described by Power and Barrowcliff.[4c] The yield was 82%; it boiled at 217° (23 mm.) (Power reports 211° at 19 mm.); n^{25}_D, 1.4577.

Hydnocarpyl Alcohol.—A reduction of 30 g. of ethyl hydnocarpate with sodium and absolute alcohol was carried out in a manner similar to that of the reduction of ethyl chaulmoograte.[2c] The product was isolated in the same way. The yield was 12 g. (50%) of product boiling at 199.5° (14 mm.); m. p., 23°; n^{25}_D, 1.4733.

Anal. Subs., 0.8019 g., made up to 15 cc. in $CHCl_3$ gave a rotation of +3.52° in a 1-dcm. tube; $[\alpha]_D = +67.8°$.

Subs., 0.1206, 0.1058: CO_2, 0.3574, 0.3092; H_2O, 0.1358, 0.1188. Calcd. for $C_{16}H_{30}O$: C, 80.59; H, 12.69. Found: C, 80.85, 80.34; H, 12.60, 12.60.

Hydnocarpyl Bromide.—From 10 g. of hydnocarpyl alcohol by the method used for chaulmoogryl bromide (VanDyke and Adams), 8.5 g. (70%) of product boiling at 206–210° (14 mm.) was obtained; m. p., 1°; n^{25}_D, 1.4871.

Anal. Subs., 0.5859, made up to 15 cc. in $CHCl_3$ gave a rotation of +1.56° in a 1-dcm. tube; $[\alpha]_D = +40.0°$.

Subs., 0.1597, 0.1960: 11.03, 12.69 cc. of 0.05 *N* $AgNO_3$. Calcd. for $C_{16}H_{29}Br$: 26.56. Found: 26.38, 26.27.

Homohydnocarpic Acid, II.—A mixture of 6 g. of hydnocarpyl bromide in 20 cc. of alcohol and 1.5 g. of potassium cyanide in 2 cc. of water was refluxed for 15 hours. Water was added and the nitrile extracted with ether. No attempt was made to purify the nitrile on account of the small quantity of material available. It was hydrolyzed by refluxing overnight with 10% aqueous alcoholic sodium hydroxide. Water was added, the solution acidified with hydrochloric acid and the resulting acid crystallized from 80% alcohol. A yield of 2 g. of pure product melting at 56–57° was obtained.

Anal. Subs., 0.5033 g., made up to 15 cc. in $CHCl_3$ gave a rotation of +1.87° in a 1-dcm. tube; $[\alpha]_D = +56.7°$.

Subs., 0.2345, 0.2111: 8.78, 7.89 cc. of 0.1 *N* NaOH. Calcd. for $C_{17}H_{30}O_2$; neut. equiv., 266.3. Found: 267.1, 267.6.

Summary

1. Homohydnocarpic acid and homochaulmoogric acid have been prepared by converting the hydnocarpyl alcohol and chaulmoogryl alcohol into the corresponding bromides, then into the cyanides and finally hydrolyzing the latter products.

2. Chaulmoogrylamine has been prepared by the condensation of chaulmoogryl bromide with potassium phthalimide and hydrolyzing the condensation product, and chaulmoogryldiethylamine has been prepared by condensing the bromide with diethylamine.

3. These substances and chaulmoogrylacetic acid have been tested for bactericidal action against *B. leprae.*

4. A number of cyclopentane, cyclohexane and cinnamic acids and benzene derivatives have been tested for bacteriological effect on *B. leprae.*

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE MECHANISM OF REACTION BETWEEN THIONYLANILINE AND ORGANOMAGNESIUM HALIDES

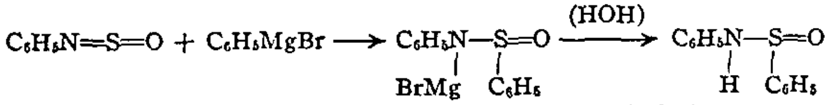
BY HENRY GILMAN AND HARRY L. MORRIS[1]

RECEIVED JUNE 10, 1926 PUBLISHED SEPTEMBER 4, 1926

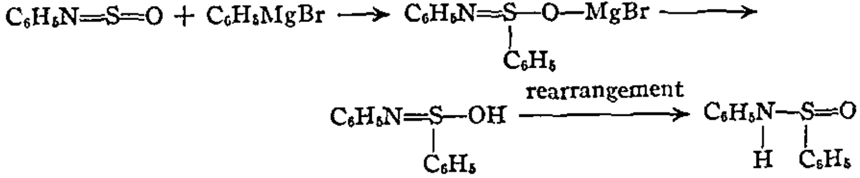
Introduction

Thionylamines ($RN{=}S{=}O$) are related structurally to ketenes ($R_2C{=}C{=}O$), isocyanates ($RN{=}C{=}O$) and isothiocyanates ($RN{=}C{=}S$). These different classes of compounds have a pair of terminal cumulated unsaturated groups and take part in a number of reactions in common. It has been proved that the ketenes,[2] isocyanates[3] and isothiocyanates[3] react under ordinary conditions with but one molecular proportion of RMgX compound. Addition is restricted exclusively to the terminal unsaturated group, the R of the RMgX compound attaching itself to carbon and the —MgX to oxygen and to sulfur, respectively.

When thionylaniline, C_6H_5NSO, the most representative of thionylamines, is treated with typical organomagnesium halides but one molecule of the latter adds under ordinary conditions and anilides of sulfinic acids result. These sulfinanilides may have resulted by either of two mechanisms, depending on whether addition took place at the $—N{=}S—$ (I) or at the $={S}{=}O$ (II) group, as follows.



$$C_6H_5N{=}S{=}O + C_6H_5MgBr \longrightarrow C_6H_5\underset{BrMg}{\underset{|}{N}}{-}\underset{C_6H_5}{\underset{|}{S}}{=}O \xrightarrow{(HOH)} C_6H_5\underset{H}{\underset{|}{N}}{-}\underset{C_6H_5}{\underset{|}{S}}{=}O \qquad (I)$$



$$C_6H_5N{=}S{=}O + C_6H_5MgBr \longrightarrow C_6H_5N{=}\underset{C_6H_5}{\underset{|}{S}}{-}O{-}MgBr \xrightarrow{(HOH)}$$

$$C_6H_5N{=}\underset{C_6H_5}{\underset{|}{S}}{-}OH \xrightarrow{\text{rearrangement}} C_6H_5\underset{H}{\underset{|}{N}}{-}\underset{C_6H_5}{\underset{|}{S}}{=}O \qquad (II)$$

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[1] This paper is an abstract of a thesis submitted by H. L. Morris in partial fulfilment of the requirements for the degree of Master of Science in Chemistry at Iowa State College in 1922. A preliminary account of the work was presented at the Birmingham, Alabama, meeting of the American Chemical Society, April 5–6, 1922 and abstracted in *Science*, **56**, 54 (1922).

[2] Gilman and Heckert, THIS JOURNAL, **42**, 1010 (1920).

[3] Gilman and Kinney, *ibid.*, **46**, 493 (1924).

A standard method for determining the mode of reaction is to treat the addition compound, prior to hydrolysis, with a so-called reliable[4] reagent which will replace the —MgBr group by another, in order to give a compound that lends itself to ready identification. Unfortunately, none of the compounds used for this purpose in earlier studies[2,3] succeeded in replacing the —MgX group. This indicated strongly that the —MgX group had attached itself to oxygen, because the study of isocyanates[3] showed that the —OMgX group was decidedly inert in the sense that the —MgX attached to oxygen would not undergo ordinary replacement reactions. Furthermore, advantage was taken of a recent extensive study[5] of new reagents for characterizing simpler —OMgX groups and none of these was found effective. Inasmuch as these reagents replace the —MgX group attached to nitrogen in a variety of compounds[5] and do not replace generally the —MgX attached to oxygen, it must be concluded that the —MgX group has added to oxygen and not to nitrogen. Accordingly, the mechanism of reaction is that of Scheme II.[6]

The amides of sulfinic acids are new compounds. Unsuccessful attempts have been made to prepare them from sulfinic anhydrides[7] and from the acid chlorides of sulfinic acids.[8] The identity of benzene-sulfinanilide[9] obtained from thionylaniline and phenylmagnesium bromide was confirmed, in part, by a mixed-melting-point determination with the same compound obtained by the slow addition of benzene-sulfinic chloride to a highly diluted cold ether solution of aniline. This anilide, as well as other amides, was prepared by v. Braun and Kaiser[10] in a related manner.

Recently, Sonn and Schmidt[11] reported on the preparation of sulfinani-

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[4] Unpublished results of completed work have shown that the several reagents commonly used to replace the —MgX group do not lead to ambiguous results due to rearrangements. These studies have been made with groups, particularly the benzyl group, that are known to undergo rearrangement in some reactions of the Grignard reagent.

[5] Unpublished work.

[6] This conclusion, which admittedly is based on negative results, finds admirable confirmation in the electronic interpretation of terminal cumulated unsaturated groups as proposed by Carothers, THIS JOURNAL, 45, 1734 (1923); 46, 2226 (1924).

Aliphatic diazo compounds (R_2CN_2) and diazo-imides (RN_3), although having in one of their generally accepted formulas a pair of terminal cumulated unsaturated groups do not behave towards the Grignard reagent like the ketenes, isocyanates and thionylamines. Instead, addition takes place at the terminal nitrogen atom alone. Preliminary mention of this work with reference to an abstract is contained in Ref. 22 of a paper by Gilman and Pickens [THIS JOURNAL, 47, 2406 (1925)].

[7] Knoevenagel and Polack, *Ber.*, 41, 3323 (1908).

[8] Hilditch and Smiles, *Ber.*, 41, 4113 (1908).

[9] Gilman and Morris, *Science*, 56, 54 (1922). See Ref. 1 of this paper.

[10] v. Braun and Kaiser, *Ber.*, 56, 549 (1923).

[11] Sonn and Schmidt, *Ber.*, 57, 1355 (1924). The final publication of our work was withheld until the study of the —OMgX compounds (Ref. 5) had been completed in order to ascertain more definitely the mode of reaction.

lides from the reaction between thionylaniline and the Grignard reagent. Where the same Grignard reagents were used, the results are in complete agreement with ours. However, in some cases we obtained aniline salts of sulfonic acids ($RSO_3H.C_6H_5NH_2$) instead of the sulfinanilides. Several experiments showed that these salts were readily formed by the hydrolysis and oxidation, particularly in wet ether solution, of the sulfinanilides. It is possible to avoid the formation of the aniline sulfonates by rapidly working up the product of hydrolysis of thionylaniline and Grignard reagent.

Experimental Part

Thionylaniline was prepared according to the method described by Michaelis.[12] A 10% increase in yield over that obtained by him is to be attributed in large part to the use of continuous stirring.

In the several experiments an emulsion of the thionylaniline in ether was added slowly to a well-stirred, cold solution of the Grignard reagent, of which about a 10% excess was generally used.[13] After the thionylaniline had been added, the mixture was refluxed for about one hour and then hydrolyzed by being poured slowly into an iced 5% solution of hydrochloric acid.[14] The solid reaction products were obtained in the customary manner from the dried ether solution.

Reaction with Phenylmagnesium Bromide.—From 35 g. or 0.25 mole of thionylaniline and a slight excess of phenylmagnesium bromide, there was obtained 28 g. or an 80% yield of benzene-sulfinanilide. When recrystallized from boiling ether it melted[15] at 115°.

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[12] Michaelis, *Ann.*, **274**, 173 (1893); *Ber.*, **24**, 745 (1891).

[13] The yields of some Grignard reagents have been determined by Gilman and McCracken [THIS JOURNAL, **45**, 2462 (1923)]. In some later experiments the RMgX compound was added to the thionylaniline until a positive color test for an excess of the Grignard reagent was obtained [Gilman and Schulze, *ibid.*, **47**, 2002 (1925)]. In this way it was determined that about one molecular equivalent of RMgX compound was required. Unless the thionylaniline is freshly distilled, an excess of RMgX is necessary because of the hydrolysis of thionylaniline (see Ref. 12 of this paper) to aniline and sulfur dioxide, both of which react with RMgX compounds.

The protracted digestion of thionylaniline with an excess of phenylmagnesium bromide at about 100° gives apparently intractable oils. However, when the reaction is carried out with an excess of phenylmagnesium bromide at the boiling point of ether, benzene-sulfinanilide is obtained in good yields.

Phenylisocyanate and -isothiocyanate, when refluxed for several hours at about 100° with an excess of phenylmagnesium bromide, give a good yield of a yellow compound that melts at 143°. This compound has not as yet been identified, although it undergoes quantitative acid hydrolysis into aniline and phenylfluorene.

[14] Sonn and Schmidt (Ref. 11) hydrolyzed their reaction mixtures with ammoniacal ammonium chloride in order to avoid the extensive decomposition products they obtained when hydrolysis was effected by acids. In our work no marked decomposition was noticed when hydrolysis was carried out by the careful addition to iced dil. hydrochloric acid.

[15] The melting point reported by v. Braun and Kaiser (Ref. 10) is 112–114° and that

Anal. Calcd. for $C_{12}H_{11}ONS$: S, 14.74. Found: 14.96, 14.89.

When warmed for 30 minutes with very dilute sulfuric acid the sulfinanilide gave aniline and benzenesulfinic acid. V. Braun and Kaiser[10] reported deep-seated decomposition and no smooth hydrolysis when the sulfinanilide was heated with acids. They recommended hydrolysis by dil. alcoholic alkali solution and this, too, was found effective after we had first hydrolyzed the substance by acids.

The identity of benzene-sulfinanilide was further confirmed by a mixed-melting-point determination with the compound obtained by the reaction between benzenesulfinic chloride and aniline. This sulfinanilide was prepared by the slow addition of benzenesulfinic chloride in petroleum ether to a highly diluted, well stirred solution of aniline in ether, kept cold by a freezing mixture. The compound so obtained, after two recrystallizations from ether, melted sharply at 116°.[15]

Attempted Replacement Reactions of the —OMgX Group.—After the customary reaction between thionylaniline and phenylmagnesium bromide, most of the ether was replaced by toluene, an equivalent amount of triphenylchloromethane was added and the mixture refluxed at about 100° for two hours. On hydrolysis there was obtained a 62.5% yield of benzene-sulfinanilide in addition to some triphenylcarbinol that undoubtedly owed its formation to the hydrolysis of triphenylchloromethane.

In like manner, when the reaction mixture in ether was refluxed with an equivalent of diethyl sulfate, there was obtained subsequent to hydrolysis a 75% yield of benzenesulfinanilide.

When the reaction mixture in ether was refluxed, prior to hydrolysis, with benzoic anhydride,[16] the following products were obtained after acid hydrolysis of the entire mixture: benzanilide, dibenzoylaniline, $C_6H_5N(COC_6H_5)_2$, aniline benzenesulfonate and an unidentified compound, m. p. 160°, that contained nitrogen but no sulfur. In another experiment, the ether was replaced largely by benzene prior to refluxing with benzoic anhydride and, in addition to a 30% yield of benzanilide, some benzene-sulfinanilide was obtained. Acetic anhydride under corresponding conditions gave largely the aniline-benzenesulfonate. When bromomethyl-ethyl ether, $BrCH_2OC_2H_5$, was used in an attempt to replace the —MgBr attached to oxygen, the largest part of the reaction mixture consisted of apparently intractable oils.

Aniline-benzenesulfonate.[16]—The aniline-benzenesulfonate previously described in connection with the benzoic and acetic anhydride experiments was identified by its neutralization equivalent (calcd.: 251; found: 254, 255.5) and by a mixed-melting-point determination with an authentic specimen.[17] It was possible to get needles melting at 243° by precipitation caused by the addition of ether to an alcoholic solution.

In the experiments involving the reaction between thionylaniline and phenylmagnesium bromide, it was observed that no aniline-benzenesulfonate was formed when benzene was used as a solvent. However, the salt appeared to form quite readily with ether as a solvent. This suggested the following qualitative experiments.

Benzene-sulfinanilide was allowed to stand in wet ether, anhydrous ether, a mixture of dry ether and dry benzene, and in dry benzene. The characteristic needles of aniline-benzenesulfonate began to form in the wet ether solution after a few hours;

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reported by Sonn and Schmidt (Ref. 11) is 112–113°. The temperatures recorded in this paper are uncorrected. Benzene-sulfinanilide melts at 110° but a mixed-melting-point determination with benzene-sulfinanilide shows a depression.

[16] Work of F. Schulze.

[17] Gericke, *Ann.*, **100**, 207 (1856). Norton and Westenhoff, *Am. Chem. J.*, **10**, 129 (1888). Knight, *ibid.*, **19**, 151 (1897).

the dry ether and dry ether-benzene solutions yielded a smaller amount of the salt after several days; the dry benzene solution gave the salt after ten days. It is known that benzene-sulfinanilide is hydrolyzed readily by merely warming with water. What very probably happens is that the sulfinate is first hydrolyzed and subsequently the sulfinic acid is oxidized to sulfonic acid which then forms a salt with aniline. Possibly the ether may accelerate the hydrolysis by its greater miscibility with water, and also accelerate the oxidation by the intermediate formation of an ether peroxide.[18]

Reaction with *p*-Tolylmagnesium Bromide.—The reaction was carried out in a manner identical with that of phenylmagnesium bromide However, the product was permitted to undergo hydrolysis and oxidation to aniline *p*-toluenesulfonate. It melted at 230° when precipitated from an alcoholic solution by the addition of ether. No depression was noted when a mixed-melting-point determination was made with an autentic specimen prepared according to Norton and Otten[19]

Reaction with *n*-Butylmagnesium Bromide.—The product obtained after hydrolysis of material from the thionylaniline and *n*-butylmagnesium bromide experiment was allowed to stand in ether for a longer time than usual. It was best obtained in a pure state by adding ether to an ethyl acetate solution. After three recrystallizations it melted sharply at 159°. Solubility tests indicated that it was an aniline-sulfonate and not the *n*-butylsulfinanilide. Analysis confirmed its identity as aniline-*n*-butylsulfonate. The yield was 80%, starting with 0.25 mole of thionylaniline.

Anal. Calcd. for $C_{10}H_{17}O_3NS$: C, 51.94, H, 7.36; N, 6.06; S, 13.85; H_2O, 7.79. Found. C, 51.6, 51.6; H, 7.7, 7.7; N, 6.21, 6.55; S, 14.26, 14.29, 14.16; H_2O, 7.69.

The loss of water was determined by heating at 105° for three hours. It is interesting that Norton and Westenhoff[17] observed no dehydration of aliphatic amine salts of benzenesulfonic acid when heated in a vacuum at 110°. The dehydration product of aniline-*n*-butylsulfonate is being investigated.

Reaction with Benzylmagnesium Chloride.[16]—Twenty-eight and a half g. or a 61.6% yield of benzyl sulfinanilide was obtained from 0.2 mole of thionylaniline and an excess of benzylmagnesium chloride. When crystallized from benzene it melts at 144–145°, which agrees with the melting point given by Sonn and Schmidt.[11] After standing overnight in wet ether the sulfinanilide is converted to white, flaky crystals that melt between 230° and 235° when crystallized from alcohol. This compound is soluble in water, slightly soluble in alcohol and insoluble in ether. Very probably it is aniline-benzylsulfonate, and like the other aniline sulfonates, owes its formation to the hydrolysis and oxidation of the sulfinanilide.

Reaction with Cyclohexylmagnesium Bromide.—The product obtained from the reaction between thionylaniline and cyclohexylmagnesium bromide was soluble in dry ether and in hot benzene, but insoluble in hot ethyl acetate. After two crystallizations from hot benzene it melted sharply at 214°. The yield of aniline-cyclohexylsulfonate was 75%, starting with 0.25 mole of thionylaniline.

Anal. Calcd. for $C_{12}H_{19}O_3NS$: S, 12.45; H_2O, 7.0. Found: S, 12.15, 12.33; H_2O, 6.85.

The water was determined by drying for three hours at 105°.

Summary

Thionylaniline adds one molecule of an RMgX compound at the S=O group to give sulfinanilides in good yields. The sulfinanilides undergo

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[18] Gilman and Wood, This Journal, 48, 806 (1926). See, particularly, Ref. 9.

[19] Norton and Otten, *Am. Chem. J.*, 10, 140 (1888).

ready hydrolysis and oxidation, particularly in wet ether solution, yielding aniline salts of the corresponding sulfonic acids.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

OPTICALLY ACTIVE DIAZO COMPOUNDS

III. A CRYSTALLINE, ALICYCLIC DIAZO ESTER

BY FORREST EVERETT KENDALL[1] WITH WILLIAM ALBERT NOYES

RECEIVED JUNE 14, 1926 PUBLISHED SEPTEMBER 4, 1926

Levene and La Forge[2] first discussed the possibility of an asymmetric aliphatic diazo group. They obtained a crystalline diazo compound that very probably contained such a group, but they could not demonstrate this, as the compound contained other asymmetric carbon atoms.

In 1918 Levene[3] assumed optically active diazo groups and a Walden inversion in the treatment of an aliphatic amino group with nitrous acid. Some years before, Potter[4] and one of us had observed a Walden inversion, involving the shift of a methyl group, on treatment of an alicyclic amino acid with nitrous acid.

In 1920 Marvel and Noyes[5] attempted unsuccessfully the preparation of an aliphatic diazo compound in which the only asymmetric carbon atom was the one attached to the diazo group.

Levene and Senior and Levene and Mikeska[6] had also been working on the problem and the latter obtained an active compound with a small rotatory power. In the latter paper they reaffirm their belief in the optical activity of the diazo group, based on the different products obtained by the action of nitrous acid on glucose-aminic and manosaminic esters. As they did not isolate the two isomeric diazo compounds, such a conclusion does not seem to be entirely valid.

Chiles and Noyes[7] obtained six optically active diazo compounds in which the asymmetric carbon atom was combined with the diazo group. Levene and Mikeska[8] have confirmed their work in part, but have found some differences.

In the discussion of Levene and in the earlier discussion by the senior

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[1] Abstract from a thesis presented to the Graduate Faculty of the University of Illinois in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Levene and La Forge, *J. Biol. Chem.*, **21**, 347 (1915). Dr. Levene and the senior author of this paper discussed the possibility of such asymmetry in March, 1915.

[3] Levene, *J. Biol. Chem.*, **36**, 89 (1918).

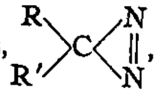
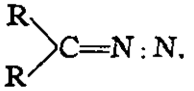
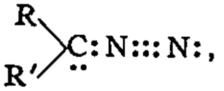
[4] Noyes and Potter, THIS JOURNAL, **34**, 1067 (1912).

[5] Marvel and Noyes, *ibid.*, **42**, 2259 (1920).

[6] Levene and Mikeska, *J. Biol. Chem.*, **45**, 592 (1921); **52**, 485 (1922).

[7] Marvel with Noyes, THIS JOURNAL, **42**, 2259 (1920). Chiles and Noyes, *ibid.*, **44**, 1798 (1922).

[8] Levene and Mikeska, *J. Biol. Chem.*, **55**, 795 (1923).

author, it has been assumed that the optical activity of the diazo compounds may be explained either by the Curtius,  $\begin{matrix}R\\R'\end{matrix}\!\!>\!C\!<\!\begin{matrix}N\\\|\\N\end{matrix}$, or the Angeli-Thiele formula,  $\begin{matrix}R\\R\end{matrix}\!\!>\!C{=}N:N$. If atoms held together by a pair of shared electrons are only potentially, and not actually, positive and negative,[9] the optical activity of diazo compounds cannot be explained by the Curtius formula. The work of Staudinger[10] on the addition of phosphines to aliphatic compounds has demonstrated that the Angeli-Thiele straight-chain formula is more probable. We may write this formula  $\begin{matrix}R\\R'\end{matrix}\!\!>\!\underset{\cdot\cdot}{C}:N:::N:$, indicating that the pair of electrons between the carbon and nitrogen atoms is shared by the two atoms, forming a covalence, while the lower pair belongs exclusively to the carbon and forms a polar valence corresponding to the polar valence of the acid radical in aromatic diazonium salts. Such a compound might be optically active in the same manner as the optically active sulfonium compounds of Smiles, of Pope and Peachey and of Pope and Neville,[11] in which one of the valences is a similar polar valence on the sulfur atom.[12] This formula bears some resemblance to the formula $R_2{=}C::N::N::$, proposed by Langmuir,[13] but the latter formula ignores the very important distinction between shared and unshared electrons in their ability to balance the positive charges of the nuclei of atoms. This distinction will be discussed in a future paper.

The pair of unshared electrons on the carbon atom may be the reason why aliphatic diazo compounds are so sensitive to hydrogen ions and why they racemize so easily.

The rotation of the active diazo compounds thus far obtained is so small that some critics think that it may be due to impurities which it is impossible to remove from such unstable substances. While we are convinced that this criticism is not warranted, it seems very desirable to se-

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[9] See Noyes, This Journal, 45, 2959 (1923); *Trans. Faraday Soc.*, 19, 476 (1923); *Bull. soc. chim.*, 34, 418 (1924); *Ber.*, 57, 1236 (1924).

[10] Staudinger, *Helvetica Chim. Acta*, 5, 75 (1922).

[11] Smiles, *J. Chem. Soc.*, 77, 1174 (1900). Pope and Peachey, *ibid.*, 77, 1072 (1900). Pope and Neville, *ibid.*, 81, 1552 (1902).

[12] It should be noticed that the polar valence of the carbon atom assumed here is negative, while that of the sulfur atom in the sulfonium compounds is positive. This is because either four unshared electrons or four pairs of shared electrons are required in the outer shell of a carbon atom to balance the positive charge of the nucleus, while six unshared electrons or six pairs of shared electrons are required to balance the charge of the nucleus of a sulfur atom. This important principle, which has not been explicitly stated before, will be made the subject of a subsequent paper.—W. A. Noyes.

[13] Langmuir, This Journal, 42, 285 (1920).

cure compounds with a higher rotatory power and also compounds that can be purified by crystallization. We have obtained such compounds from both *cis*- and *trans*-aminocamphonanic acid. As these substances contain two asymmetric carbon atoms, it is necessary to secure the diazo compound from both forms in order to establish the optical activity of the diazo group. Thus far we have secured only a small amount of the diazo compound from the *trans* form, and the evidence is incomplete, but it seems desirable to report now on the work already finished.

The decomposition of the two aminocamphonanic acids with nitrous acid has been very thoroughly investigated by Skinner and Noyes,[14] and the products are partly different, but there is no conclusive proof that the diazo compounds are an intermediate step in the decomposition. Even if they are such a step, as seems probable, they may racemize or undergo inversion during their decomposition.

Noyes and Coss[15] have shown that a diazo compound is an intermediate in the formation of the bishydrazone of camphonanic ester discovered by Noyes and Taveau.[16] We find that two molecular proportions of the diazo compound described in this paper decompose practically quantitatively on standing a short time at ordinary temperatures, giving one molecular proportion of the bishydrazone and one of nitrogen. The formula for the diazo compounds given here indicates that the reaction is closely analogous to the coupling reactions of aromatic diazonium compounds. When benzene diazonium chloride couples with dimethylaniline, a hydrogen ion from the latter combines with the chloride ion and the outer nitrogen atom of the diazonium group attaches itself to the position left vacant, the diazonium group rearranging at the same time to the azo group:

$$C_6H_5\underset{\ddot{Cl}}{\underset{.}{N}}{:}{:}{:}N + H{\cdot}C_6H_4N(CH_3)_2 = C_6H_5{-}N{=}N{-}C_6H_4N\text{-}(CH_3)_2 + HCl.$$

In the formation of the bishydrazone one molecule of the diazo compound loses a molecule of nitrogen and the outer nitrogen atom attaches itself in the place of the diazo group. The compound then rearranges to the bishydrazone, $R{=}\underset{\cdot\cdot}{C}{:}N{:}{:}{:}N{:} + R{=}\underset{\cdot\cdot}{C}{:}N{:}{:}{:}N{:} = R{=}C{:}{:}N{:}N{:}{:}C{=}R + N_2$. This formula also gives a very simple explanation for the Walden rearrangements referred to above. The substituting atom or group attaches itself to the unshared electrons of the carbon atom. This will give anoptical inversion.

In addition to the work of Taveau and Coss referred to, Ross[17] also attempted the preparation of the diazo compound from *cis*-aminocamphonanic acid, but the desired compound was not isolated.

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[14] Skinner and Noyes, THIS JOURNAL, 39, 2692 (1917). Skinner, *ibid.*, 45, 1498 (1923).

[15] Noyes and Coss, *ibid.*, 42, 1280 (1920).

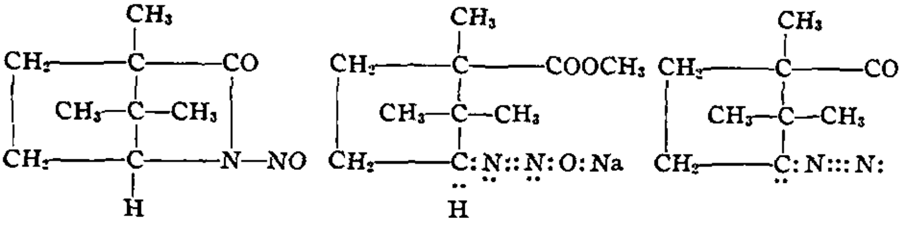
[16] Noyes and Taveau, *Am. Chem. J.*, 32, 287 (1904).

[17] Ross, *Master's thesis*, University of Illinois, 1925.

In the present work it was finally obtained in a crystalline form as follows.

Two g. of the nitroso-anhydride dissolved in 50 cc. of anhydrous ether was treated with 0.25 molecular proportion of sodium methylate in methyl alcohol at —20°. The yellow color of the nitroso solution gradually changed and at the end of an hour a deep red solution showing a blue fluorescence in certain lights was obtained.

Our interpretation of the reaction is that the sodium atom of the sodium methylate adds to the oxygen of the nitroso group and the methoxy group to the carbon of the carbonyl. This is accompanied by the formation of a double union between the two nitrogen atoms. Sodium hydroxide then splits off, a triple union forms between the nitrogen atoms and a polar valence on the carbon atom that has lost hydrogen.



The relations of the electrons concerned with the formation of the diazo group are indicated in the last two formulas.

The solution was washed with water to remove alcohol and sodium hydroxide, both of which catalyze the decomposition of the diazo compound, and was dried by cooling to —80° to freeze out the water. The anhydrous salts usually employed for drying liquids cause a rapid decomposition of the diazo compound. The solution was concentrated to a volume of 5 cc. under reduced pressure in a stream of dry air, free from carbon dioxide. Carbon dioxide also causes rapid decomposition. Upon cooling this solution to —80°, rouge-red, hexagonal crystals separated. The solvent was removed with an inverted filter and the crystals were dried on a porous plate and placed in a vacuum desiccator. When they were allowed to warm to 10° they gradually melted with the evolution of nitrogen and later formed a white solid that was shown to be the bishydrazone of Noyes and Taveau; 0.2209 g. of the diazo compound was placed in a stoppered tube and allowed to warm to room temperature. The crystals melted with evolution of nitrogen and at the end of 48 hours had solidified, giving a white, waxy solid; m. p., 45°; loss in weight, 0.0172 g., or 7.78%. This indicated a 90% conversion into the bishydrazone and a 10% conversion into nitrogen-free unsaturated compounds. Unsaturation was shown by the action toward potassium permanganate. The solid after two crystallizations from a mixture of ether and petroleum ether melted at 99°, the value given by Taveau for the bishydrazone.

Because of the instability of the diazo compound, the crystals were kept, and all work with them was carried out in a cold room where the temperature was below freezing. The crystals melted quite sharply at 30° when heated rapidly in a capillary tube. The material was analyzed for diazo nitrogen by decomposing it with dil. sulfuric acid and measuring the nitrogen evolved. The analysis of the first crystals obtained gave 11.7% of nitrogen; calcd., 14.3%. This indicated a diazo content of 82%. By recrystallizing five times from 5cc. portions of ether, an analysis of 13.9% of nitrogen, indicating 97.5% of the diazo compound, was obtained.

The specific rotation of the diazo compound was obtained in two ways. The crystalline solid was weighed and dissolved in ether and the rotation of the solution measured. As the impurities contained in the compound, principally the bishydrazone, had very low rotations, the rotation observed was considered to be due entirely to the diazo compound and a correction made according to the diazo content; 0.2124 g. containing by analysis 82% of diazo compound, dissolved in 25 cc. of ether gave a rotation of +3.28°, $[\alpha]_D$ = +336°; corrected for diazo content, $[\alpha]_D$ = 405°; 0 2174 g. containing by analysis 93% dissolved in 25 cc. of ether gave a rotation of +3.36°; $[\alpha]_D$ +386°; corrected for diazo content, $[\alpha]_D$ = 415°. The diazo compound was analyzed for carbon and hydrogen in the ordinary manner.

Table I

Summary of Analyses

Preparation	Carbon, %	Hydrogen, %	Nitrogen, %	$[\alpha]_D$	$[\alpha]_D$ corr. to % of diazo
1	..	..	11.7	+376°	+405°
2	..	..	13 3	+386°	+415°
3	61.13	7.60	13 9	+367°	+378°
4	..	..	12.9	+405°	+450°
5	..	..	13.2	+362°	+400°
6	61.9	8.91	13.3	....	....
7	62.0	8.53	13.8	+396°	+410°
8	..	..	13.4	+384°	+409°
Calcd.	61.2	8.16	14.3	....	....
				Av.	+409°

As the values obtained for the specific rotation of the diazo compound varied considerably, due probably to the gradual decomposition of the compound in the ether solution, a second method of obtaining the specific rotation was devised. The rotation of an ether solution was determined and the solution then analyzed by introducing a measured portion into a mercury eudiometer and decomposing with methylsulfuric acid. The volume of the gas evolved was measured and corrected for the vapor pressure of ether. By keeping the temperature low, so as to reduce the vapor pressure of the ether, accurate values were obtained. As the solution used was more impure than that obtained from the crystalline substances, the rotation of the solution after decomposition was subtracted from the rotation observed.

Table II

Summary of Rotations of Diazo Solution

Preparation	Diazo ester per cc., g.	Obs. $[\alpha]_D$	Obs $[\alpha]_D$ after decompn.	$[\alpha]_D$
1	0.0172	+ 8.10°	+0.67°	+432°
2	.0143	+ 6.82°	+0.70°	+427°
3	.0284	+13.15°	+1.04°	+426°
4	.0203	+10.31°	+1.28°	+445°
			Av.	+433°

In order to decide definitely whether this high rotation is due in part to the diazo group or was due entirely to the other asymmetric carbon atom it was necessary to obtain the diazo compound from the isomeric *trans*-aminocamphonanic acid. This compound does not form an anhydride, so the method used for the *cis* compound could not be used. Attempts to use von Pechmann's[18] method, by the action of alkali upon the nitroso derivative of an acylamine, failed because we were unable to prepare the nitroso derivative of either the benzoyl or formyl compound. Werner[19] has shown that primary alkyl ureas give nitroso derivatives upon treatment with nitrous acid and that these decompose with alkali giving diazo compounds. $CH_3—NH=CO—NH_2 \rightleftarrows CH_3—NH—C(OH)=NH \xrightarrow{HNO_2} CH_3—N(NO)—C(OH)=NH \xrightarrow{KOH} CH_2=N\equiv N + CO_2 + NH_3$. *sec*-Butyl urea and other secondary alkyl ureas investigated did not give nitroso derivatives with nitrous acid but decomposed, giving the corresponding isocyanates in 50% yields. The disubstituted secondary alkyl ureas, however, gave nitroso derivatives that decomposed with alkali to give the desired diazo compounds.

The disubstituted urea from methyl-*trans*-aminocamphonanate was obtained in two ways.

First, by treating the ethereal solution obtained by the action of nitrous acid upon the monosubstituted urea with methyl-*trans*-aminocamphonanate the disubstituted urea was obtained. This substance is insoluble in ether, dilute acids and cold alcohol. It is somewhat soluble in hot alcohol and crystallizes from it in long, silky needles; m. p., 305° (corr.). Second, it was prepared by treating an ethereal solution of the amine ester with an equivalent amount of phosgene in toluene After standing for two hours the precipitated "di-urea" and amine hydrochloride are filtered off. The hydrochloride is removed by washing with water and the "di-urea" recrystallized from hot alcohol. The material prepared in this way had the same melting point as that described above.

Anal. Subs., 0.1503: CO_2, 0.3492; H_2O, 0.1230. Calcd. for $C_{21}H_{36}O_5N_2$; C, 63.85; H, 9.09. Found. C, 63 35; H, 9.08.

One g. of the "di-urea" was suspended in ether and treated with nitrous anhydride to form the nitroso derivative. The ether solution of the nitroso derivative was treated with sodium methylate at —20° and allowed to stand for one hour. At the end of that time the solution was washed with cool water and dried by cooling to —80° and filtering off the ice that had been frozen out. The rotation of the solution for sodium light was determined and found to be +1.28°. The solution was analyzed for diazo nitrogen by the method already described. Five cc. of the solution gave 1.8 cc. of nitrogen over ether at 745 mm. and 0°. This is equivalent to 0.0116 g. of diazo ester, or a concentration of 0.0023 g. per cc.

After decomposition the rotation of the solution was +0 48°. This gave a specific rotation $[\alpha]_D = +558°$ for the solution of the diazo compound. As the solution after decomposition had a rotation considerably above any obtained in later determinations, it was thought that the difference between the rotation of the solution before and after decomposition would give a more accurate measure of the rotation of the compound; $[\alpha]_D = +348°$ (corr.).

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[18] von Pechmann, *Ber.*, 27, 1888 (1894).

[19] Werner, *J. Chem. Soc.*, 115, 1093 (1919).

Two more preparations of the diazo solution were made in the same way; $[\alpha]_D$ = 415° and 430°.

The rotatory dispersion of ether solutions of both the *cis* and *trans* forms of the diazo compound were measured. The lines of the mercury-vapor arc were used as a source of light. Measurements were made in a very sensitive, three-shade universal polarimeter.

TABLE III

AVERAGE VALUES FOR SPECIFIC ROTATION OF DIAZO ESTERS

Wave length, Å.	6152	5780	5461	4900	4350
From *cis* compound	+260°	+510°	+785°	−80°	−590°
From *trans* compound	+240°	+535°	+810°	−85°	−475°

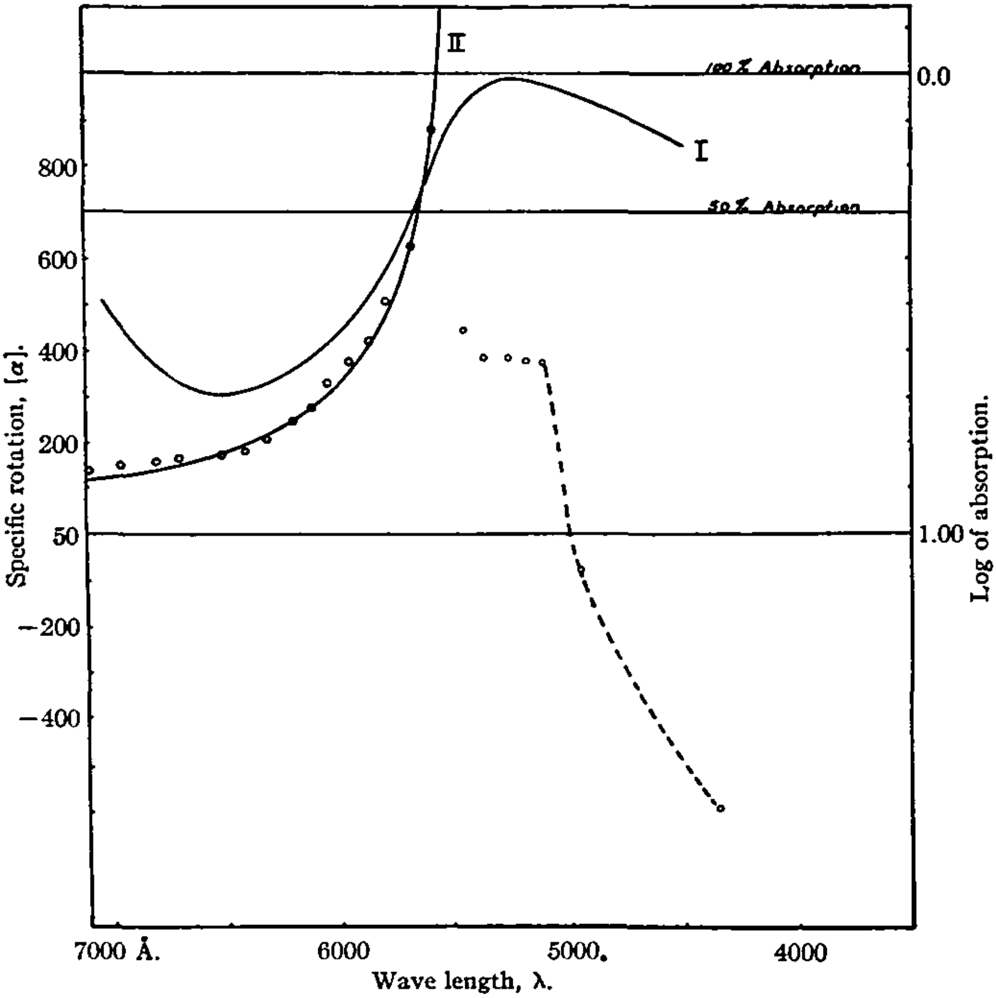

Fig. 1.—Rotatory dispersion of methyl γ-diazo-camphonanate. I. Absorption curve; C = 0.0014 g./cc. in ether. II. Calculated from $[\alpha] = 26/(\lambda^2 - 0.53^2)$. Circles; experimental values of [α].

According to Lowry and Walker,[20] those terms of Drude's equation, $[\alpha] = [K_0/(\lambda^2-\lambda_0^2)] + [K_1/(\lambda^2-\lambda_1^2)] + \ldots$, that contain the character-

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[20] Lowry and Walker, *Nature*, 113, 565 (1924).

istic frequencies of any particular group in a molecule represent the contribution of that group to the rotation of the compound. The absorption of the diazo compound was measured in a spectrophotometer; it was shown that there was an absorption band that centered at about $\lambda = 5300$ Å. This band is without question due to the diazo group. The rotatory dispersion curve (Fig. 1) for the red and yellow part of the spectrum agreed very closely with the curve $[\alpha] = K/(\lambda^2-\lambda_0^2)$, where $\lambda_0 = 0.53$ micron and $K = 26$, indicating that this part of the curve is due largely to the asymmetry of the carbon atom bearing the diazo group. (See Possibility 3 in the discussion below.) The deviation of the curve from that calculated may represent the effect of the other asymmetric carbon.

Discussion

So far as the primary purpose of our investigation is concerned, the results must be considered as still inconclusive. There seem to be three possibilities.

1. The rotation caused by the asymmetry of the carbon atom bearing the diazo group may be small, as it is with all similar groups thus far studied. The determinations of the rotation, especially that of the *trans* compound, are not sufficiently accurate to settle this point.

2. The diazo group may racemize as soon as it is formed and the rotation may be due exclusively to the carbon atom bearing the methocarboxyl group. The fact that Skinner found, in part, the same products from the action of nitrous acid on the *cis*- and *trans*-amino esters, points somewhat to this conclusion.

3. Because of the other asymmetric carbon atom the *cis* form of the diazo compound may be formed both from the *cis* anhydride and the *trans* "di-urea." The dispersion curves point to this conclusion, as mentioned above.

Skinner found by the decomposition of the *cis*-aminocamphonanic acid 40 parts of hydroxy to 60 parts of unsaturated esters; from the *trans* ester, 60 of hydroxy and 40 of unsaturated esters. The decomposition of our diazo compound prepared from the *cis* anhydride has given approximately the same proportions of the two classes of products that Skinner found from the *cis*-amino ester. Also, it has given none of the *cis*-camphonolic ester which he found among the products from the decomposition of the *trans* compound. These facts point to either the first or third possibility. A decision between these may be possible by studying the decomposition products of the diazo compound from the *trans* "di-urea." This will be undertaken, but the problem is extremely difficult and it may not be possible to secure enough of the necessary materials.

Summary

1. A crystalline diazo compound has been obtained by treating the nitroso derivative of the anhydride of *cis*-aminocamphonanic acid with sodium methylate and crystallizing the product from ether at —80°.

2. The compound melts at 30°. Its specific rotation, $[\alpha]_D$, is about 420°.

3. The rotatory dispersion of the compound is large, ranging from +260° through +785° to —590°. The dispersion agrees closely with the values calculated from Drude's equation.

4. A diazo compound has also been prepared, in small amounts and in a less pure condition, from the "di-urea" *trans*-aminocamphonanic acid. Its properties agree, roughly, with those of the diazo compound from the *cis* acid but the evidence on this point is incomplete.

5. It has been pointed out that an electronic interpretation of the Angeli-Thiele formula for the aliphatic diazo compounds shows a close analogy between these compounds and the aromatic diazonium compounds.

6. The diazo compound passes almost quantitatively into the bis-hydrazone of camphonanic acid on standing for a short time. This reaction is closely analogous to the coupling reactions of aromatic diazonium compounds.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE]

PECTIC ACIDS

BY E. K. NELSON

RECEIVED JUNE 14, 1926 PUBLISHED SEPTEMBER 4, 1926

F. Ehrlich and R. V. Sommerfeld, in their exhaustive investigation on the constitution of the pectic substances of the sugar beet,[1] apply the term "pectin" to the material, usually called "protopectin," which is not soluble in cold water, but is dissolved by hot water.

According to Ehrlich and Sommerfeld, this "pectin" is hydrolyzed by hot water into "hydropectin," which can be separated by 70% alcohol into soluble araban and the calcium-magnesium salt of pectic acid which is not dissolved. On treating this salt with hydrochloric acid in the cold and precipitating with alcohol they obtain the free pectic acid $C_{43}H_{62}O_{37} + 10H_2O$ which, after hydrolysis for several hours with 2% hydrochloric acid on the water-bath, yields methyl alcohol, acetic acid, arabinose, galactose, an insoluble digalacturonic acid (A) and a soluble digalacturonic acid (B). They conclude that beet pectic acid is a triacetyl-arabino-galacto-dimethoxy-tetragalacturonic acid. The digalacturonic acids are formed from two molecules of galacturonic acid by the elimination of water between the aldehyde groups and hydroxyl groups of the adjacent molecule. The insoluble modification (A) has the formula $C_{10}H_{14}O_8(COOH)_2H_2O$.

Wichmann and Chernoff in their method for determining pectic acid

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[1] Ehrlich and Sommerfeld, *Biochem. Z.*, 168, 263–323 (1926).

in fruit products,[2] which is used as a check on the pectin determination, employ a treatment similar to that used by Ehrlich in his preparation of digalacturonic acid (A) except that they use an alkaline hydrolysis with dil. sodium hydroxide solution, followed by boiling for five minutes with dil. hydrochloric acid. The present investigation was conducted for the purpose of establishing the identity of Wichmann and Chernoff's pectic acid with digalacturonic acid (A).

One hundred g. of citrus pectin was dissolved in water and hydrolyzed with dil. sodium hydroxide solution for 15 minutes at room temperature, then acidified with hydrochloric acid in suitable excess and boiled for five minutes according to Wichmann and Chernoff's procedure. The insoluble precipitate was filtered and redissolved in dil. sodium hydroxide solution and the operation was repeated. The acid was filtered off, washed with water until the filtrate gave a negative reaction for chloride, and finally with alcohol and ether. The resulting material was dried in a vacuum desiccator; yield, 39 g.

One g. requires 52.9 cc. of 0.1 *N* sodium hydroxide solution for neutralization. Ehrlich states that his digalacturonic acid (A) required 54.0 cc.; calcd. for $C_{10}H_{14}O_8(COOH)_2 + H_2O$: 54 cc.

One g. of the acid was neutralized with sodium hydroxide solution and diluted to 100 cc. This solution was used for the determination of specific rotation; $[\alpha]_D = +289.5°$. Ehrlich reports +272° to +285°.

Mr. C. F. Gersdorff of this Bureau kindly made an analysis of the acid, with the following results.

Anal. Subs. (dried at 110°), 0.3339: H_2O, 0.1500; CO_2, 0.4818. Calcd. for $C_{12}H_{16}O_{12} + H_2O$: H, 4.86; C, 38.92. Found: H, 4.99; C, 39.35.

On hydrolysis of digalacturonic acid with dilute sulfuric or oxalic acid at 2 to 3 atmospheres (130–140°), Ehrlich[3] obtained galacturonic acid which responded to the tests given by glucuronic acid (reduction of Fehling's solution in the cold, and the orcinol, resorcinol, phloroglucinol and naphthoresorcinol reactions) and yielded a characteristic cinchonine salt crystallizing in fine, pointed needles and melting, with decomposition, at 158°. Under the conditions described above, Wichmann and Chernoff's pectic acid yielded an acid which is easily soluble in alcohol and water but is unstable, easily oxidizing or polymerizing to a black, tarry or humin-like material. It gives the naphthoresorcinol reaction and reduces Fehling's solution in the cold. Efforts to produce a crystalline cinchonine salt by saturating its solution with cinchonine were unsuccessful. This salt was prepared through the barium salt as follows.

The acid solution, after autoclaving, was neutralized with barium hydroxide solution and filtered from barium sulfate or oxalate. The filtrate was concentrated somewhat in a vacuum-distillation outfit and then treated with an excess of alcohol which precipitated the barium salt as a yellow, water-soluble powder.

Anal. Calcd. for $Ba(C_6H_9O_7)_2$: Ba, 26.23. Found: 25.92.

The cinchonine salt was prepared by treating an aqueous solution of the barium

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[2] Wichmann and Chernoff, *J. Assoc. Official Agr. Chem.*, **8**, 129 (1924).

[3] Ehrlich, *Chem. Z.*, **41**, 198 (1917).

salt with the calculated amount of cinchonine sulfate, filtering the solution and concentrating the filtrate in a vacuum distilling flask.

The salt crystallized slowly from the concentrated solution, and most of the impurities could be removed by washing with a little cold alcohol. While this salt is easily soluble in warm water or alcohol, it crystallizes with some difficulty. The crystals are not immediately soluble in *cold* water or alcohol; hence, it was purified by washing with a little cold alcohol.

The cinchonine salt crystallizes in fine, pointed needles and melts with decomposition at 159–160°; Ehrlich reports 158°. The alcoholic filtrate from the barium salt was evaporated. It gave a small amount of a brown, amorphous substance from which no galactose could be isolated.

The pectic acid described by Wichmann and Chernoff is, therefore, digalacturonic acid (A), the characteristic nucleus of pectic substances.

Conclusion

The pectic acid obtained by Wichmann and Chernoff's method for determining pectin in fruit products is identical with the digalacturonic acid (A) of Ehrlich and Sommerfeld.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NEBRASKA]

DICARBOXY-PHENYLARSONIC ACIDS

I. 2,3-DICARBOXY-PHENYLARSONIC ACID AND ITS ANHYDRIDE

BY CLIFF S. HAMILTON AND RALPH FRAZIER

RECEIVED JUNE 21, 1926 PUBLISHED SEPTEMBER 4, 1926

Very little study has been made of phthalic acids containing an arsonic acid group on the nucleus. Only isophthalarsonic acid or 2,4-dicarboxyphenylarsonic acid has been prepared and no derivatives have been studied. Michaelis prepared the acid by oxidizing 2,4-dimethylphenylarsonic acid with potassium permanganate in alkaline solution,[1] but no reference can be found in the literature to dicarboxy-phenylarsonic acids that have been obtained by the introduction of the arsonic group into a phthalic acid nucleus.

It was of interest, therefore, to prepare 2,3-dicarboxy-phenylarsonic acid from *o*-phthalic acid. This was accomplished by first nitrating *o*-phthalic acid, then reducing the nitro compound to 3-amino-*o*-phthalic acid, and finally introducing the arsenic by means of Bart's method.[2]

The properties of 2,3-dicarboxy-phenylarsonic acid are very similar to those of monocarboxy-phenylarsonic acids. It has no melting point up to 270°, decomposition starting at approximately 220°. It is very slightly soluble in either hot or cold alcohol, insoluble in ether, but highly soluble in either hot or cold water. The free acid may be recrystallized as colorless

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[1] Michaelis, *Ann.*, **320**, 335 (1902).

[2] Bart, Ger. pat., 250,264 (1910); *Ann.*, **429**, 55 (1922).

needles from water or glacial acetic acid, but best by dissolving in hot water and adding an excess of hydrochloric acid.

The anhydride of 2,3-dicarboxy-phenylarsonic acid was formed when the free acid was heated at high temperatures. When the anhydride was condensed with resorcinol it formed a fluorescent compound resembling fluorescein. Condensation with phenol resulted in the formation of a solution resembling phenolphthalein, colorless in acid solution and pink in alkaline solution.

Further study of dicarboxy-phenylarsonic acids and their derivatives is now being carried out in this Laboratory.

Experimental Part

3-Nitro-*o*-phthalic Acid.—This was prepared by heating 185 g. of phthalic anhydride with a mixture of 175 cc. of nitric acid (d., 1.42) and sulfuric acid (d., 1.84), on a steam-bath for three hours.[3] The mixture was poured into water which dissolved the more soluble 4-isomer and left 3-*o*-phthalic acid as light yellow crystals. These were filtered off and washed with 300 cc. of water. The crude 3-*o*-phthalic acid was then distilled with benzene until the distillate was clear, to remove the excess of water and nitric acid; m. p., 198°; yield, 80–85%.

3-Amino-*o*-phthalic Acid.—This was made by the reduction of the corresponding nitro compound with tin and hydrochloric acid, while the temperature was kept at 20° and the mixture stirred in order to prevent local heating. Decomposition resulted when the temperature was allowed to rise above 30°.[4] The amino compound crystallized from the reducing mixture as the hydrochloride. It was dissolved in water and recrystallized by the addition of an equal volume of concd. hydrochloric acid. The portion remaining in solution was recovered by saturating the solution with dry hydrogen chloride. The product thus obtained was used in the preparation of the arsonic acid, after being dried under reduced pressure over sodium hydroxide to remove the excess of hydrochloric acid; yield, 45–50%. Because of conflicting data on this compound it was analyzed.

Anal. Subs., 0.5162, 0.4937: AgCl, 0.3527, 0.3433. Subs., 0.5314, 0.5018: 32.6, 31.65 cc. of 0.0714 *N* HCl. Calcd. for $C_8H_8O_4NCl$: N, 6.43; Cl, 16.30. Found: N, 6.14, 6.31; Cl, 16.47, 16.54.

2,3-Dicarboxy-phenylarsonic Acid.—Twenty-five g. of the hydrochloride of 3-amino-*o*-phthalic acid was dissolved in 500 cc. of water containing 23 cc. of hydrochloric acid (d., 1.18) and diazotized with 9 g. of sodium nitrite in 100 cc. of water, the temperature being kept below 0°.

The diazo solution was slowly added, during constant stirring, to a solution containing 75 g. of sodium arsenite, 5 g. of copper sulfate, and 25 g. of sodium hydroxide in 600 cc. of water, the temperature being allowed to rise to 20°. After the diazo solution had all been added, the mixture was stirred for one hour. It was then boiled until nitrogen was no longer evolved, made acid to Congo red paper, and evaporated to dryness. The residue was dried at 150° for several hours to remove the excess of acid, pulverized, and the soluble inorganic salts were extracted with 100 cc. of water at 0°. The residue was then treated with 100 cc. of water and 20 cc. of ammonium hydroxide and the mixture filtered. When the filtrate was made acid to Congo red paper and an excess of 20 cc. of hydrochloric acid was added, the *o*-phthalarsonic acid separated as light

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[3] Littmann, THIS JOURNAL, **47**, 1980 (1925).

[4] Bogert and Jouard, *ibid.*, **31**, 484 (1909).

brown crystals. The acid was purified by dissolving in boiling water, decolorizing with charcoal and recrystallizing by adding one-fourth the volume of hydrochloric acid. The free acid separated as colorless crystals which decomposed without melting when heated; yield, 50–55%. A sample, recrystallized from water, was dried at 98°.

Anal. Subs., 0.2043, 0.2043: 29.0, 29.3 cc. of 0.0490 N I soln. Calcd. for $C_8H_7O_7As$: As, 25.86. Found: 25.61, 25.85.

The Neutral Trisodium Salt was prepared by dissolving 2,3-dicarboxy-phenylarsonic acid in the calculated amount of 0.5 N sodium hydroxide solution and filtering into absolute alcohol. The salt separated as an oil and was crystallized under reduced pressure.

Anal. Subs. (dried at 120° for five hours), 0.1990, 0.2047: 23.3, 23.9 cc. of 0.0483 N I soln. Calcd. for $C_8H_4O_7AsNa_3$: As, 21.07. Found: 21.14, 21.13.

The anhydride of 2,3-dicarboxy-phenylarsonic acid was prepared by heating the free acid for one week at 200°.

Anal. Subs., 0.2050, 0.2090: 31.1, 32 cc. of 0.0483 N I soln. Calcd. for $C_8H_5O_6As$: As, 27.57. Found: 27.53, 27.78.

Summary

2,3-Dicarboxy-phenylarsonic acid has been made and studied, and its neutral sodium salt and anhydride have been prepared. A further study of the dicarboxy-phenylarsonic acids and their derivatives is now being carried out in this Laboratory.

LINCOLN, NEBRASKA

[Contribution from the Chemical Laboratory of Princeton University]

THE REACTIVITY OF HALOGENATED ETHERS
I. HALOGENATED DIETHYL ETHERS AND ZINC

By F. Neher and C. L. Fleece

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The halogenated ethers resemble the alkyl halides in their reactivity to such reagents as metals, alcoholic and aqueous potassium hydroxide, lime and sodium ethylate. But the reactions of the alkyl halides, as shown by Nef,[1] vary remarkably with temperature, concentration and the nature of the solvent, poor yields and a mixture of products being obtained. The reagent may remove two atoms of the halogen or the halogen acid; unsaturated products may be formed or addition products. An investigation of the behavior of zinc with alcoholic solutions of the halogenated ethers discussed in this paper and others to follow has shown that these compounds are much better suited to a study of the mechanism of the reactions of organic compounds of the halogens since the metal may have an entirely selective action and remove halogen or halogen acid, exclusively. A general mechanism for this selective action has been found by an examination of tetra-, tri-, di- and monochlorodiethyl ethers and some new bromo and bromochloro ethers.

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[1] Nef, *Ann.*, 298, 330 (1897).

The reactions of the halogenated ethers are more readily interpreted in terms of electron displacement than are those of the alkyl halides and unsaturated hydrocarbons, since the negative alkoxy groups affect the mobilities of both the halogen and the hydrogen atoms of the alkyl radical. Also, there is a sharp differentiation in properties between two isomeric halogenated ethers depending upon the location of halogens on α or β carbon atoms. One may be very unstable and active, the other extremely stable and of very low reactivity.

α,β,β,β-Tetrachlorodiethyl Ether.—Neher and Foster[2] found that an alcoholic solution of this ether reacts with granulated zinc to give a quantitative yield of β,β-dichlorovinyl-ethyl ether; $CCl_3CHClOC_2H_5 + Zn = CCl_2{:}CHOC_2H_5 + ZnCl_2$. No hydrogen is liberated and none of the alcohol adds to the vinyl ether unless the solution is heated. Six molecular proportions of alcohol were used, the mixture cooled under the tap and allowed to stand overnight. Later experiments, the results of which have not been published, showed that dichloro-acetal is the chief product when the mixture is heated for several hours on the steam-bath.

To establish the various conditions under which the dichlorovinyl ether may be formed, the work was repeated. It was found that good yields of the unsaturated ether could be obtained with various concentrations of the alcohol solution and at temperatures from about 10° to 50°. Under a wide range of conditions the action of zinc was found to be entirely selective and only chlorine was removed. The removal of hydrogen chloride from the tetrachloro ether would have yielded either trichlorovinyl ether or trichloro-acetal (by the addition of alcohol to the vinyl ether), but there was no indication of the formation of either compound. This reaction of the saturated ether, in which two atoms of chlorine are removed and no hydrogen chloride, is unlike the reactions of the alkyl halides in which zinc usually removes the halogen acid.

α,β,β-Trichlorodiethyl Ether.—This ether was prepared by the addition of dry hydrogen chloride to β,β-dichlorovinyl ether; $CCl_2{:}CHOC_2H_5 + HCl = CHCl_2CHClOC_2H_5$. A very pure product was obtained by this method since no by-products were formed; no decomposition occurred during the saturation and samples showed only slight coloration after standing for several months. This compound was found to be more reactive toward zinc than the tetrachloro ether. It was thought that this ether would react with zinc to form either the dichlorovinyl ether, $CCl_2{:}CHOC_2H_5$, or the chlorovinyl ether, $CHCl{:}CHOC_2H_5$, depending upon the removal of hydrogen chloride or two atoms of chlorine by the zinc. Experiments showed, however, that neither is obtained. Zinc removed hydrogen chloride, exclusively, under all conditions and never two atoms of chlorine, but dichlorovinyl ether could not be obtained, although over 20

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[2] Neher and Foster, This Journal, 31, 413 (1909).

different combinations of solvents, concentrations and temperatures were tried with the trichloro ether. In all experiments in which the zinc reacted with the ether alone, or dissolved in indifferent solvents such as carbon tetrachloride, ligroin, toluene or acetone, the reactions were violent, and rapid decomposition could not be prevented by cooling the mixtures to 0°. The resulting products were chiefly tarry masses and no definite compounds could be isolated. When the trichloro ether was dissolved in six molecular proportions of alcohol, however, good yields of dichloro acetal were obtained, hydrogen being evolved throughout the experiments.

$$CHCl_2CHClOC_2H_5 + {}^1/_2\ Zn + C_2H_5OH = CHCl_2CH(OC_2H_5)_2 + {}^1/_2\ ZnCl_2 + {}^1/_2\ H_2$$

The solution of the tetrachloro ether used by Neher and Foster contained six molecular proportions of alcohol, also, and was allowed to react at room temperatures. They obtained no dichloro-acetal under these conditions but did get good yields of the dichlorovinyl ether. When the trichloro ether loses hydrogen chloride the same dichlorovinyl ether is released that is formed by the removal of two chlorine atoms from this tetrachloro ether, but the formation of dichloro-acetal by alcohol addition could not be prevented even by cooling the solution with an ice-and-salt freezing mixture and adding the zinc very gradually.

The Formation of Vinyl Ethers and Acetals.—In an attempt to find a general mechanism for the selective removal of the halogen or the halogen acid from halogenated ethers and to explain the conditions under which vinyl ethers or acetals are formed, this reaction has been applied to a number of halogenated ethers containing from one to four halogen atoms in the alkyl radical. The following general facts have been determined. (1) Zinc will remove halogen atoms from both carbon atoms only when there are three atoms of the halogen on the beta carbon atom of the halogenated diethyl ether and one or more on the alpha carbon. *In alcoholic solution*, good yields of vinyl ethers are obtained by this action. (2) The halogen acid will be removed if an alpha carbon atom carries a halogen atom and there are *one or more hydrogen atoms on the beta carbon atom*. This has been found true for ethers carrying one, two and three hydrogen atoms on the beta carbon atom and one halogen atom on the alpha carbon atom. The product, however, is always an acetal instead of a vinyl ether when the saturated ether loses the halogen acid in the presence of alcohol. (3) A hydrogen atom on an alpha carbon atom is never removed by zinc if there is halogen on this carbon. If there is hydrogen on the beta carbon atom, however, it is always removed with the halogen of the alpha carbon atom, although the beta carbon may carry one or two atoms of the halogen.

The reaction of the trichloro ether mentioned above is typical of all other halogenated diethyl ethers that lose the halogen acid and form acetals in the presence of alcohol. The following examples are similar to the tetrachloro ether reaction and they show that vinyl ethers may be formed in the presence of alcohol if they are released by the removal of two halogen atoms instead of the halogen acid.

α-Chloro-β,β,β-tribromodiethyl Ether.—This compound was made by the action of phosphorus pentachloride on bromal alcoholate in ether solution; $CBr_3CH(OH)OC_2H_5 + PCl_5 = CBr_3CHClOC_2H_5 + POCl_3 + HCl$. An attempt had been made to prepare the corresponding tetrabromo ether by the action of phosphorus pentabromide on the bromal alcoholate, but with no success. The chief product was bromoform instead of the tetrabromo ether. The latter was finally prepared by converting the chlorotribromo ether into dibromovinyl ether by the zinc reaction and adding bromine to the unsaturated ether.

β,β-Dibromovinyl-ethyl Ether.—An alcoholic solution of the chlorotribromo ether, prepared as described above, reacted with zinc to form dibromovinyl-ethyl ether. No hydrogen was evolved; this indicated that only halogen atoms were removed by the zinc and not the halogen acid; there was no evidence of alcohol addition to form an acetal. $CBr_3CHClOC_2H_5 + Zn = CBr_2{:}CHOC_2H_5 + ZnClBr$.

α,β,β,β-Tetrabromodiethyl Ether.—This ether was prepared by carrying bromine vapor into the cold dibromovinyl ether with a stream of carbon dioxide, the bromine adding as calculated; $CBr_2{:}CHOC_2H_5 + Br_2 = CBr_3CHBrOC_2H_5$. The tetrabromo ether is much less stable than the corresponding tetrachloro ether and there is considerabledecom position when it is distilled at reduced pressure. An alcoholic solution of this ether reacted with granulated zinc to form the vinyl ether; as in the case of the tetrachloro ether, two halogen atoms were removed by the zinc and no hydrogen bromide. No hydrogen was evolved and no acetal formation was detected; $CBr_3CHBrOC_2H_5 + Zn = CBr_2{:}CHOC_2H_5 + ZnBr_2$.

α-Bromo-β-bromo-β,β-dichlorodiethyl Ether.—By the addition of bromine to dichlorovinyl ether, this dibromodichloro ether was obtained and its reactivity to zinc tested; $CCl_2{:}CHOC_2H_5 + Br_2 = CCl_2BrCHBrOC_2H_5$. The compound reacted with zinc at room temperature to form an unsaturated product that was found to be chiefly $CCl_2{:}CHOC_2H_5$ mixed with a small amount of $CClBr{:}CHOC_2H_5$, but the lack of hydrogen formation and the properties of the product showed that the zinc had removed two halogen atoms and not a halogen acid.

Theoretical Part

Four examples have been given of the conversion of halogenated ethers into vinyl ethers by the removal of two halogen atoms by zinc. Other halogenated ethers, such as trichloro ether, dichloro ether and monochloro ether, lose the halogen acid under similar conditions and in alcoholic solution, but the products are acetals. The preparation of dichlorovinyl ether from tetrachloro ether and dichloro-acetal from trichloro ether may be taken as typical of the two reactions. Possible explanations are as follows. (1) The formation of the dichloro-acetal may be due to a direct action between the alpha chlorine atom of the trichloro ether and alcohol in which hydrogen chloride is removed. This reaction is not probable since the alpha chlorine atoms of both trichloro ether and tetrachloro ether show the same degree of reactivity and a direct action with alcohol at a low temperature would not be expected in the one case when it does not occur in the other even at a much higher temperature. Trichloro ether[3] and tetrachloro ether[4] do not react with alcohol at room temperatures, but both ethers form acetals if boiled for several hours with alcohol. When tetrachloro ether reacts with zinc and alcohol, however, no trichloro-acetal is formed. The formation of the acetal in the one case and not in the other could not be due to the catalytic action of zinc or zinc chloride since these substances were present in both reactions. (2) Since zinc removes chlorine from one ether and hydrogen chloride from the other, the halogen acid may act as a condensing agent in the acetal formation; but no evidence for this condensing action could be found. The evolution of hydrogen throughout the experiments with trichloro ether indicated that, if any free hydrogen chloride was formed, the amount was very small. Also, hydrogen chloride is absorbed readily by dichlorovinyl ether at room temperatures and alcohol is not. Various tests were made to determine whether or not the presence of hydrogen chloride could cause alcohol addition to the vinyl ether. An alcoholic solution of tetrachloro ether was treated with zinc by the method already described and the solution of dichlorovinyl ether and zinc chloride separated from the zinc. Dry hydrogen chloride was run into samples of this solution and the amounts absorbed, determined by weighings. The quantities absorbed varied from about 5 to 50% of that calculated for the saturation of the dichlorovinyl ether present. If the conversion of the trichloro ether into dichloro-acetal was due to a condensation produced by the hydrogen chloride that might have been present, then the dichlorovinyl ether solutions should have converted entirely in to the acetal. But all the samples tested contained unchanged vinyl ether, the amounts depending upon the quantities of hydrogen chloride that had been run in. The hydrogen chloride had merely added to form trichloro-ether. (3) The acetal formation may be explained by the electronic condition of the vinyl ether at the instant it is released by the removal of hydrogen chloride from a saturated ether.

Reactions of the Double Bonds of Vinyl Ethers.—W. H. Carothers[5] pointed out that the reactions of the double bond could be accounted for by assuming a displacement of electrons to produce parts more or less polar,

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[3] Oddo and Mameli, *Gaz. chim. ital*, [ii] 33, 412 (1903).

[4] Wurtz and Vogt, *Z. Chem.*, 7, 680 (1871).

[5] Carothers, THIS JOURNAL, 46, 2226 (1924).

applying a more general idea proposed by Lewis, Lowry, Noyes[6] and others. He represents active propylene as $CH_3—\overset{*}{C}H—CH_2$, the starred carbon being the "deficient" or positive carbon to which the bromine of hydrogen bromide will attach. The hydrogen of the halogen acid is then drawn to the free electron pair of the negative carbon. A similar addition would be expected if the active propylene molecules are assumed to have the electronic structure $CH_3{:}\underset{\ddot{H}}{C}{:}\underset{\ddot{H}}{\ddot{C}}{:}H$, using the Lewis notation.

If such a state of polarization precedes the addition of a polar molecule, such as hydrogen bromide, to a double bond, then the removal of a halogen acid from a compound should leave the unsaturated product, momentarily, highly polarized. A double bond produced in this manner should be less stable and more likely to form addition products with other polar molecules at the instant it is released than if the unsaturated compound were formed by the removal of two negative atoms. The electronic states of dichlorovinyl ether when formed by the removal of chlorine and hydrogen chloride, respectively, from two chlorinated ethers may be indicated as follows.

$$Cl_2\overset{Cl}{\ddot{C}}{:}\overset{Cl}{\ddot{C}}HOC_2H_5 + Zn = ZnCl_2 + Cl_2\dot{C}{:}\dot{C}HOC_2H_5 = Cl_2C{:}{:}CHOC_2H_5 \qquad (1)$$

$$Cl_2\overset{H}{\ddot{C}}{:}\overset{Cl}{\ddot{C}}HOC_2H_5 + {}^1/_2\,Zn = {}^1/_2\,ZnCl_2 + H + Cl_2\ddot{C}{:}CHOC_2H_5 \qquad (2)$$

$$Cl_2\ddot{C}{:}CHOC_2H_5 + H{:}OC_2H_5 = Cl_2\overset{H}{\ddot{C}}{:}\overset{OC_2H_5}{\ddot{C}}HOC_2H_5$$

In Reaction 1 the vinyl ether would not be released in a condition favorable to alcohol addition unless heated; in Reaction 2 its electronic condition would make it more unstable and more reactive to other polar molecules. These reactions illustrate the general mechanism by which zinc removes the halogen or halogen acid from such compounds. The alpha hydrogen atoms never are removed by the metal if there is a halogen atom on this carbon; but beta carbon atoms lose hydrogen, although there may be available halogen atoms present, as in the case of the trichloro ether shown above. The beta hydrogen atoms, therefore, must be nearer the ionic condition and will be released more readily by the transfer of an electron from the zinc. This will leave the hydrogen-bonding pair on the beta carbon atom, as shown above, and the mechanism of alcohol addition will be similar to the addition of a halogen acid to a polarized molecule of an unsaturated hydrocarbon.

Experimental Part

The Action of Zinc on α,β,β,β-Tetrachlorodiethyl Ether.—To test the Neher and Foster reaction, in which zinc removed two chlorine atoms and

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[6] (a) Lewis, This Journal, **38**, 762 (1916). (b) Lowry, *J. Chem. Soc.*, **123**, 822 (1923). (c) Noyes, This Journal, **45**, 2959 (1923).

no hydrogen from this tetrachloro ether, the work was repeated at different temperatures and concentrations. Alcohol concentrations varied from two to six molecular proportions and temperatures from 20° to 75°. The solutions were allowed to stand overnight, water was added, the product distilled with steam, dried and redistilled; b. p., 144°. No hydrogen was evolved, showing that no trichlorovinyl ether was formed. The yields ranged from 70 to 90%, the higher yields being obtained with about six molecular proportions of alcohol. The method was later adopted by a manufacturing chemist for preparing dichlorovinyl ether in quantity.

Preparation and Properties of α,β,β-Trichlorodiethyl Ether.—This ether has been prepared by the chlorination of ether,[3,7] by the addition of chlorine to β-chlorovinyl ether[8] and by heating dichloro-acetal with phosphorus pentachloride.[9]

This ether was prepared in a very pure state by running hydrogen chloride into dichlorovinyl ether until a sample tested with bromine showed that saturation was complete. In one experiment, 95 g. of the unsaturated ether required seven hours' running of the hydrogen chloride for saturation. The temperature rose to 35° and remained near this point until saturation was complete. Carbon dioxide was passed through the product until the odor of hydrogen chloride was no longer noticeable. The ether had a rather pleasant odor, similar to that of tetrachloro ether, and was perfectly clear. One hundred and seventeen g. of the trichloro ether was obtained before distillation, the calculated amount being only 115 g. This indicated that the hydrogen chloride had added quantitatively, the extra 2 g. being hydrogen chloride still in solution and not removed by the carbon dioxide. The ether distilled at 77–80° (32–34 mm.); at atmospheric pressure it boiled at 173–175°, chiefly near 174°. In the preparations referred to, Oddo and Mameli obtained a boiling point of 170–175°, Krey found 167° and Godefroy only 157°. The last boiling point indicates that Godefroy may have had the isomer, $CH_2ClCCl_2OC_2H_5$, since the α-substituted ethers show lower boiling points than the β. A density (25°/4°) of 1.3116 was found. Oddo and Mameli found 1.3303 at 14°.

Anal.[10] Subs., 0.1439: Calcd. for $C_4H_7OCl_3$: C, 27.06; H, 3.97; Cl, 59.94. Found: C, 27.19; H, 4.15; Cl, 59.81.

The Action of Zinc on α,β,β-Trichlorodiethyl Ether.—Granulated zinc was added to the pure ether at room temperature. There was an immediate reaction followed by rapid decomposition and an evolution of hydrogen gas. The liberation of hydrogen gas indicated the removal of hydrogen chloride by the zinc, but the dichlorovinyl ether, if formed, was decomposed. Tarry masses were left even when the experiments were repeated at 0° and with a gradual addition of the zinc. The results were the same when the ether was dissolved in 6 molecular proportions of diethyl ether, acetone, ligroin and carbon disulfide and the solutions allowed to react with zinc at room temperatures and at 0°. When the trichloro ether was dissolved in absolute alcohol, however, good yields of dichloro-acetal were obtained. In one experiment, 33 g. of trichloro-ether was dissolved in 48 g. (6 molecular proportions) of alcohol, the flask was cooled in ice

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[7] Jacobsen, *Ber.*, **4**, 217 (1871).

[8] Godefroy, *Jahresber.*, **1886**, 1173.

[9] Krey, *ibid.*, **1876**, 475.

[10] In the analyses of these halogenated ethers, carbon, hydrogen and chlorine were obtained simultaneously by a modification of the Dennstedt method to be reported later.

water and 43 g. of zinc added. The mixture was kept at about 5° until the action had subsided and then left overnight at room temperature. The alcohol was washed out with water and 27 g. of dried oil obtained. A vacuum distillation at 18–20 mm. gave 4.5 g. at 64–76°, the remainder distilling at 76–79°. The main fraction boiled at 181–184° at atmospheric pressure, this temperature agreeing with the boiling point of dichloro-acetal; yield, 78%.

Anal. Calcd. for $C_6H_{12}O_2Cl_2$: C, 38.62; H, 6.41, Cl, 37.60. Found: C, 38.02; H, 6.47; Cl, 37.91.

Preparation of α-Chloro-β,β,β-tribromodiethyl Ether.—One hundred and fifteen g. of bromal alcoholate, prepared by the addition of alcohol to bromal, was dissolved in 150 cc. of absolute ether. Eighty-five g. of phosphorus pentachloride was cooled with a freezing mixture, washed twice with cold ether and covered with 100 cc. of ether. The ethereal solution of the bromal alcoholate was then run in slowly from a dropping funnel. The flask was shaken continually and the temperature kept below 15°. Only a slight bromine coloration was noticed at the end of the reaction. The mixture was poured from the excess of phosphorus pentachloride into 1000 g. of crushed ice and stirred until most of the ice had melted. The crude ethereal solution was separated, washed several times with large volumes of water and dried with fused calcium chloride. The diethyl ester still present was distilled and the heavy oil fractionated at reduced pressure. Ninety-seven g. of the chlorotribromo ether, b. p. 117–122° (13–14 mm.), was obtained; yield, 80%. The ether boiled at 120–121.5° (corr.) (14 mm.) at atmospheric pressure, it decomposed below the boiling point; $d^{20.5}_4$, 2.2069. The molecular weight was determined by the cryoscopic method, using benzene as a solvent.

Anal. Calcd. for $C_4H_6OBr_3Cl$: Hal., 79.74. Found: 79.87.

Mol. wt. Calcd. for $C_4H_6OBr_3Cl$: 345.5. Found: 330.

Preparation of β,β-Dibromovinylethyl Ether.—Fifty-nine g. of the chlorotribromo ether, prepared as described above, was dissolved in absolute alcohol (6 molecular proportions) and 59 g. of granulated zinc added. The reaction began at room temperature and was kept below 30° by cooling under the tap. No gas was evolved and the solution remained entirely colorless. The mixture was allowed to stand for several hours at room temperature, a liter of water was added, the product distilled with steam, dried over calcium chloride and redistilled at reduced pressure. At 14.5–15 mm., 5 g. was obtained at 69–73° and 26 g. at 73–75°; yield, 78%. The product decomposed when heated at atmospheric pressure; b. p., 73–75° (corr.) (15 mm.); $d^{17.5}_4$, 1.7697

Anal. Calcd. for $C_4H_6OBr_2$: Br, 69.57. Found: 69.03.

Preparation and Properties of α,β,β,β-Tetrabromodiethyl Ether.—Twenty-five g. of the dibromovinyl ether described above was cooled in a U-tube surrounded by a freezing mixture. This tube was connected to another U-tube containing cold bromine. Bromine vapor was driven into the vinyl ether by a stream of carbon dioxide until a slight coloration indicated an excess of the bromine, this excess being absorbed by adding two or three drops more of the vinyl ether; 41.5 g. of the tetrabromo ether was obtained, the calculated amount being 42.4 g. This indicated that the bromine had added quantitatively, the slight loss in weight being due to the evaporation of some of the liquid by the rapid stream of carbon dioxide.

The ether decomposed rapidly when attempts were made to determine its boiling point. At 16 mm. it distilled at 130–140°, the distillate smelling strongly of hydrogen bromide and showing traces of an unsaturated compound. Since no solvent was used in the preparation of the ether, no by-products were formed and the bromine added quantitatively, a sample before distillation was considered as more suited to an accurate density determination and to tests with zinc; $d^{17.5}_4$, 2.2432.

Action with Zinc.—An alcoholic solution of the tetrabromo ether was tested with zinc in exactly the same manner as that described for the chlorotribromo ether. Twenty g. of the ether gave 8 g. of an unsaturated compound boiling at 76–80° (17–18.5 mm.). This indicated the formation of dibromovinyl ether, whose boiling point had been found to be 73–75° (14.5–15 mm.). Since the properties of dibromovinyl ether had been determined in the former preparation, a molecular-weight determination was made to be sure that the unsaturated compound was not tribromovinyl ether formed by the removal of hydrogen bromide by the zinc. A molecular weight of 219 was found by the cryoscopic method, using benzene as a solvent; calcd. for dibromovinyl ether, 230; for tribromovinyl ether, 309. Also, if the tribromovinyl ether had been formed the boiling point would have been much higher than that found.

Preparation and Properties of α-Bromo-β-bromo-β,β-dichlorodiethyl Ether.—Oddo and Mameli[3] prepared this ether by adding a chloroform solution of bromine to dichlorovinyl ether. Since the dichlorovinyl ether is very stable it was thought that a purer product, free of solvent and by-products, could be formed by the direct addition of bromine. Seventy g. of the vinyl ether was placed in a 500cc. flask and the bromine added through a dropping funnel. The cork carried also a thermometer, a calcium chloride tube and a tube for running in carbon dioxide. The ether was stirred by a rapid stream of carbon dioxide while the bromine was being added and the temperature was kept between 8° and 15°. A slight coloration, which indicated saturation, was removed by the addition of two or three drops of the vinyl ether. The product weighed 148 g., the calculated yield being 149.5. Distillation at 16–16.5 mm. gave 9 g. below 107° and the remainder distilled at 107–108° with only slight decomposition; yield, 93%. Decomposition was rapid when the ether was boiled at atmospheric pressure, the distillate fumed in air and decolorized a carbon tetrachloride solution of bromine. The ether boiled at 106.5–108° (corr.) (16 mm.), with little decomposition; $d_4^{18.5}$, 1.8249. Oddo and Mameli found a boiling point of 124–129° (25–30 mm.).

Anal. Calcd. for $C_4H_6OBr_2Cl_2$: H, 2.02; C, 15.9; Hal., 76.74. Found: H, 2.21; C, 15.9; Hal., 76.6.

Action with Zinc.—Thirty-nine g. of the dibromodichloro ether was dissolved in 80 cc. of absolute alcohol and 40 g. of zinc added. The action was rapid and the flask was cooled under the tap to keep the temperature below 40°. After distilling with steam and drying the oil, 16.5 g. of an unsaturated product was obtained. This was redistilled at atmospheric pressure and 11 g. collected at 143–147° and 3 g. at 147–155°; both fractions absorbed bromine readily. A few drops of the 143–147° fraction were decomposed by molten sodium and a qualitative test indicated only chlorine. Also, the unsaturation of the product and its boiling point showed it to be chiefly dichlorovinyl ether, $CCl_2{:}CHOC_2H_5$; b. p., 144 2°. The removal of a halogen acid by the zinc would have produced either a vinyl ether or an acetal containing three halogen atoms and the boiling point would have been considerably higher than that of the fractions collected. The properties of the product showed that the zinc had removed two halogen atoms and not a halogen acid, which was the sole object of the test.

Summary

Three new halogenated diethyl ethers have been prepared and their properties determined: α-chloro-β,β,β-tribromodiethyl ether, β,β-dibromovinylethyl ether and α,β,β,β-tetrabromodiethyl ether. Pure α-bromo-β-bromo-β,β-dichlorodiethyl ether has been prepared by a modification of an older method. New methods for the preparation of α,β,β-trichlorodiethyl ether and β,β-dichloro-acetal are given.

Typical examples of the reactions of alcoholic solutions of halogenated ethers with zinc are given. The action of zinc has been found to be entirely selective in the removal of two atoms of the halogen or the halogen acid from a given ether. The mechanisms of these reactions have been studied. Beta hydrogen atoms are removed by zinc more readily than beta halogen atoms, but alpha halogen atoms are much more reactive than alpha hydrogen atoms.

The removal of two atoms of a halogen from halogenated ethers in alcohol solution results in the quantitative formation of vinyl ethers but, under the same conditions, the removal of the halogen acid from halogenated ethers containing one less halogen atom in each case does not result in the formation of the same vinyl ethers, as had been expected, but of the corresponding acetals. Various tests indicated that the acetal formation was due to the alcohol addition to the unsaturated ether after the removal of the halogen acid by the direct action of zinc on the saturated ether. The assumption is made, in explaining these facts, that the removal of the halogen acid leaves the double bond of the vinyl ether in a polarized condition that is more favorable to the addition of other polar molecules, such as alcohol, than if the vinyl ether were prepared by the removal of two halogen atoms.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

ISOXAZOLINE OXIDES

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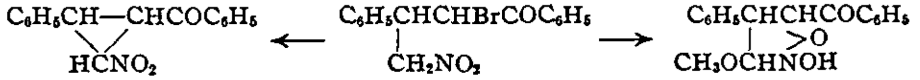
In the first paper of this series[1] it was shown that the reaction between methyl alcoholic potassium acetate and an α-bromo-γ-nitro-ketone which had no hydrocarbon residue in the γ position resulted mainly in the formation of two substances. One of these substances was the expected nitrocyclopropane derivative; the other was regarded as a methyl alcohol addition product of an isoxazoline oxide.



Most of the properties of the second product that were known at the time were expressed satisfactorily by the isoxazolidine formula, but it was not easy to account for the action of bases which readily degraded the substance into methyl alcohol, formic acid, phenylacetic acid and benzonitrile. This peculiar and unexpected reaction led to the present investigation. In order to avoid some of the difficulties encountered in the interpretation of the results of the earlier work it seemed advisable to employ, in place of

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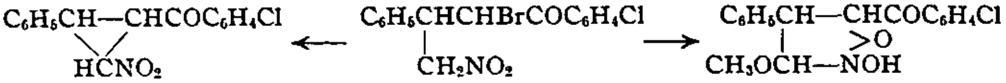
[1] Kohler, THIS JOURNAL, 46, 503 (1924).

the diphenyl compound there used, a substance in which one of the phenyl groups is marked by a substituent. The *p*-chlorophenyl compound (I) served this purpose well; it is readily prepared and, like its chlorine-free analog, it gives with potassium acetate two products of which one is a cyclopropane derivative.



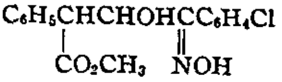
$$\begin{array}{c}C_6H_5CH{-}CHCOC_6H_4Cl\\ \diagdown\;\diagup\\ HCNO_2\\ \text{II}\end{array}\xleftarrow{\quad}\begin{array}{l}C_6H_5CHCHBrCOC_6H_4Cl\\ \quad|\\ \;CH_2NO_2\\ \quad\text{I}\end{array}\xrightarrow{\quad}\begin{array}{l}C_6H_5CH{-}CHCOC_6H_4Cl\\ \qquad\quad|\qquad >O\\ CH_3OCH{-}NOH\\ \qquad\text{III}\end{array}$$

The second product of this reaction is evidently constituted like the corresponding compound that was obtained from the chlorine-free analog, for like this it forms a green copper derivative when its ethereal solution is shaken with aqueous copper acetate, and like it also, it is degraded by concentrated alkalies into methyl alcohol, formic acid, phenylacetic acid and *p*-chlorobenzonitrile. This substance, however, cannot possibly have the structure represented by Formula III. With acetic anhydride or acetyl chloride it forms, in succession, a mono- and a diacetate. The diacetate can be hydrolyzed to a second mono-acetate and this, in turn, to the original compound. The diacetate, therefore, is formed without rearrangement and the substance must have two active hydrogen atoms—a conclusion that is quite inconsistent with Formula III.

It is not easy to see how methyl alcoholic potassium acetate can transform the bromoketone into a substance containing two active hydrogen atoms, and the behavior of corresponding ketones which have phenyl groups in the γ position gives no clue to the process. Moreover, most reagents transform the substance into oils or into products whose relation to it is remote. By cautious treatment with weak bases, however, it is possible to replace methoxyl with hydroxyl—apparently without disturbing the rest of the molecule, for the hydroxyl compound still has the peculiar power of forming a copper derivative. This hydroxyl compound is an acid from which the methoxyl compound can be regenerated by the ordinary methods of esterification. The parent substance is, therefore, a methyl ester and this, almost of necessity, is an open-chain compound.

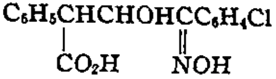
When the acid that is obtained by hydrolyzing the methoxyl compound with bases is digested with mineral acids it loses its nitrogen in the form of hydroxylamine. The result is a new acid which presumably is formed without disturbance of the rest of the molecule, because from it hydroxyl amine in a faintly alkaline solution regenerates the nitrogenous acid. This acid, therefore, contains an oximido group.

The transformations which have been described—hydrolysis to an acid, hydrolysis to a carbonyl compound and conversion into a diacetate—indicate that the substance is an open-chain compound containing a carbomethoxy, an hydroxyl and an oximido group. Assuming that the carbon chain is the same as that of the bromonitroketone, and taking account of the fact that *p*-chlorobenzonitrile is one of the degradation products, this analysis leads to Formula IV for the methoxyl compound and to Formulas V and VI for the products of hydrolysis.



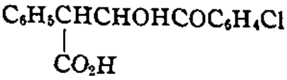
$\underset{\underset{\displaystyle CO_2CH_3}{|}}{C_6H_5CH}CHOH\underset{\underset{\displaystyle NOH}{\|}}{C}C_6H_4Cl$

IV



$\underset{\underset{\displaystyle CO_2H}{|}}{C_6H_5CH}CHOH\underset{\underset{\displaystyle NOH}{\|}}{C}C_6H_4Cl$

V



$\underset{\underset{\displaystyle CO_2H}{|}}{C_6H_5CH}CHOHCOC_6H_4Cl$

VI

All these formulas have been confirmed by synthesis. Addition of hydrogen cyanide to benzal-*p*-chloro-acetophenone gave a nitrile of which the structure was known from the method of preparation (VII). This was hydrolyzed to the corresponding acid (VIII) which was then brominated. The structure of this bromo compound likewise follows from its method of preparation (IX). When the bromoketonic acid was warmed with dil. sodium carbonate solution it gave, along with other products, the ketolic acid (VI) and this was converted into the oximido acid (V) and the oximido ester (IV) in the manner already described.

$$\underset{VII}{C_6H_5CH(CN)CH_2COC_6H_4Cl} \longrightarrow \underset{VIII}{C_6H_5CH(CO_2H)CH_2COC_6H_4Cl} \longrightarrow \underset{IX}{C_6H_5CH(CO_2H)CHBrCOC_6H_4Cl}$$

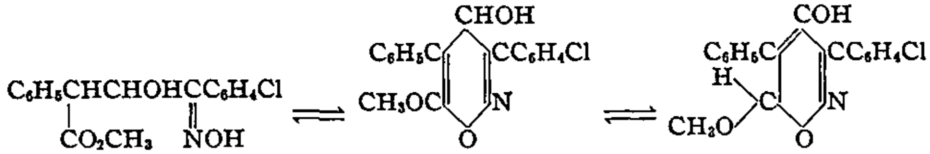
This synthesis leaves no doubt as to the structure of the oximido ester, but it gives no indication of the manner in which a mild reagent like methyl alcoholic potassium acetate converts the bromoketone into a substance that is so different from it as is the bromo ester. The process is accompanied by the formation of other products: two isomeric cyclopropane derivatives and a considerable quantity of an oil that gives the characteristic color reactions of hydroxamic acids and, on long standing, usually deposits an orthoxazine derivative. All attempts to isolate an isoxazoline oxide from the oil or to prepare such an oxide directly from the bromo compound were unsuccessful. Pyridine, which readily forms an oxide from α-bromo-γ-nitroketones that have a phenyl group in the γ position, here produces only highly colored oils. Ammonia and amines likewise eliminate hydrogen bromide but form either cyclopropanes or amorphous, acidic products. Aqueous alkalies convert most of the bromoketone into cyclopropanes but give in addition a considerable quantity of a hydroxamic acid. These results tell little about the mechanism by which the oximido ester is formed.

Most of the properties of the ester could be predicted from its structure, and therefore need no special comment here. Its ability to form a copper compound was perplexing until Feigl and his collaborators[2] announced the discovery that this is a general property of α-hydroxy-oximes. Our results confirm their conclusions in every way: the oximido acid, its ester and the corresponding amide form these extremely insoluble copper compounds; the various acetates do not.

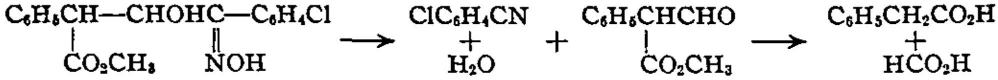
The oximido and ketolic esters are as easily acylated as the ketoses but

[2] *Feigl, Sicher and Singer, Ber.*, **58**, 2294 (1925).

they resist alkylation. With dimethyl sulfate and alkali the oximido ester gives a solid product but this, like the ester itself, contains only one methoxyl group. The composition and molecular weight of this product indicate that it is formed from the ester by loss of water and the fact that it reverts quantitatively to the oximido acid when potassium hydroxide is added to its solution in methyl alcohol confirms this relation. Since the substance forms a benzoate without losing the methoxyl group it is probably one of the modifications of an orthoxazine derivative.



The degradation of the oximido ester by alkalies which was so puzzling when the first paper was published is now readily explained. It is well known that many of the oximes which are formed by the action of alkalies on isoxazoles readily undergo cleavage and form nitriles.[3] A somewhat similar cleavage was reported by Werner and Piguet[4] who state that benzoin oxime, when treated with benzene sulfone chloride and pyridine or alkali, is smoothly cleaved into benzaldehyde and benzonitrile. We have found that the benzene sulfone chloride is not essential although it appears to facilitate the cleavage. By a corresponding reaction the oximido ester would give as primary products methylformylphenyl acetate and *p*-chlorobenzonitrile but since the aldehyde ester is likewise unstable in the presence of bases, the final products would be those actually obtained.



$$\underset{CO_2CH_3}{C_6H_5CH}-\underset{NOH}{CHOHC}-C_6H_4Cl \longrightarrow \underset{H_2O}{ClC_6H_4CN + } + \underset{CO_2CH_3}{C_6H_5CHCHO} \longrightarrow \underset{HCO_2H}{C_6H_5CH_2CO_2H +}$$

Experimental Part

The bromonitroketone used in the investigation was made by adding nitromethane to benzal-*p*-chloro-acetophenone, and brominating the product. It was known that when the mixture of stereoisomeric bromine compounds that is obtained in this way is treated with methyl alcoholic potassium acetate it gives, along with two isomeric cyclopropane derivatives, a substance that has the composition of the oximido ester.[5]

The procedure for getting this substance in quantity was as follows.

I

Fifty g. of the mixture of bromine compounds was poured into a solution of 50 g. of fused potassium acetate in 100 cc. of methyl alcohol which had been made at the boiling point and then chilled to room temperature. The thick mass was shaken briskly with occasional cooling if the reaction became too vigorous, until the bromine com-

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[3] Claisen, *Ber.*, **24**, 3904 (1891); **36**, 3672 (1903).

[4] Werner and Piguet, *Ber.*, **37**, 4309 (1904).

[5] Smith, Dissertation, Harvard University, 1920.

pound had disappeared. It was then brought to the boiling point and immediately cooled again in a freezing mixture. After 30 minutes the solid deposit was collected on a suction filter and thoroughly washed with cold methyl alcohol. Most of the cyclopropane remained on the filter, mixed with potassium bromide.

The filtrate was poured into water and the mixture thoroughly extracted with ether. The ethereal solution was freed from most of the acetic acid by extraction with sodium carbonate solution, then shaken mechanically for 24 hours with a large excess of saturated aqueous copper acetate. The precipitate of copper derivative was collected on a filter and thoroughly washed with water and hot methyl alcohol in order to remove a small quantity of cyclopropane derivative that commonly precipitated along with the copper compound. By pumping off the ether in the filtrate, decanting the clear aqueous layer and diluting the residual oil with methyl alcohol, it was usually possible to secure a small additional quantity of copper derivative.

The combined precipitates of copper compound were introduced into a separatory funnel along with a small quantity of ether and shaken with successive portions of a 1:3 hydrochloric acid until all of the copper derivative was decomposed. This procedure gave a nearly colorless ester which was washed with a mixture of ether and petroleum ether and recrystallized from methyl alcohol; yield, 7 g., or about 18%.

Anal. Calcd. for $C_{17}H_{16}O_4NCl$: C, 61.2; H, 4.8. Found: C, 61.0; H, 5.0.

Methyl α-Phenyl-β-hydroxy-γ-oximido-γ-[*p*-chlorophenyl]butyrate, III.—The ester is very slightly soluble in ether, and moderately so in boiling methyl alcohol and boiling acetone. It crystallizes in small prisms melting at 165°. Above the melting point it decomposes, *p*-chlorobenzonitrile sublimes in long colorless needles and the remainder of the molecule turns into an insoluble amorphous solid, which is evidently due to polymerization. Caustic alkalies impart a deep red color to its ethereal solution, but this soon fades; at room temperature the principal product is the corresponding acid; at higher temperatures the substance is cleaved into phenylacetic and formic acids and *p*-chlorobenzonitrile.

THE COPPER DERIVATIVE.—This is precipitated as a dark green, amorphous solid when an ethereal solution of the ester is shaken with aqueous copper acetate. As it is insoluble in water as well as in all common organic solvents it cannot be recrystallized. Specimens obtained by washing the precipitate with water and hot methyl alcohol and then thoroughly drying them showed a copper content of 15.8% instead of 15.4% as calculated; m. p., about 222°, with decomposition.

A SECOND COPPER DERIVATIVE.—A second copper derivative is formed when a suspension of the green amorphous precipitate in ether is shaken with dil. hydrochloric acid. The green powder is slowly changed into a light blue-green, crystalline solid which is very readily soluble in methyl alcohol. From its methyl alcoholic solution, ether precipitates it in fine needles that melt with decomposition at 168–170° and contain 9.5% of copper. Further treatment with acids converts the compound into the oximido ester.

Hydrolysis to the Oximido Acid, V.—One g. of the ester suspended in 2 cc. of ether was shaken with 10 cc. of a 2% solution of sodium hydroxide. The ethereal layer immediately turned red, the aqueous layer yellow. The ethereal layer retained its color until the last of the solid had disappeared, then became colorless. On evaporation it left a small quantity of *p*-chlorobenzonitrile.

The aqueous layer was thoroughly extracted with ether, then covered with ether and acidified with dil. hydrochloric acid. By vigorous shaking, the resulting milky white precipitate was quickly dissolved in the ether in order to avoid hydrolysis of the oximido group. The ethereal solution was dried, concentrated and diluted with petroleum ether; it deposited a solid that, after recrystallization from methyl alcohol, melted at 174°.

Anal. Calcd. for $C_{16}H_{14}O_4NCl$: C, 60.1; H, 4.5. Found: C, 59.9; H, 4.6.

α-Phenyl-β-hydroxy-γ-oximido-γ-[*p*-chlorophenyl]butyric Acid, V.—The acid is readily soluble in ether, moderately soluble in methyl alcohol, insoluble in petroleum ether. It crystallizes in small colorless prisms. When its ethereal solution is shaken with aqueous copper acetate it deposits an insoluble blue copper compound.

Hydrolysis to the Ketolic Acid, VI.—A very fine suspension of the oximido acid was prepared by dissolving 0.5 g. in 10 cc of 2% sodium hydroxide solution, pouring this into 100 cc. of water and adding dil. hydrochloric acid until the solution barely showed a reaction with Congo red paper. The cloudy solution gradually deposited clusters of white needles. These were washed, dried and recrystallized from ether-petroleum ether mixture.

Anal. Calcd. for $C_{16}H_{13}O_4NCl$: C, 63.1; H, 4.3. Found· C, 62.8; H, 4.5.

α-Phenyl-β-hydroxy-γ-oxo-γ-[*p*-chlorophenyl]butyric Acid, VI.—The acid is readily soluble in all common organic solvents except petroleum ether. It crystallizes in fine needles and melts at 139–140°. It is, as would be expected, unstable in alkaline solution. Thus its colorless solution in sodium hydroxide turns yellow when warmed, the acid loses water and carbon dioxide, and the solution deposits benzal-*p*-chloroacetophenone. Its solution in sodium carbonate likewise turns yellow and deposits a colorless, indifferent crystalline solid which, doubtless, is an hydroxyketone. The acid also has the reducing power characteristic of α-hydroxyketones, being readily oxidized both by permanganate and by ammoniacal silver nitrate solution

II. Synthesis of the Oximido Ester and its Hydrolysis Products

α-Phenyl-β-[*p*-chlorobenzoyl]propionitrile, VII.—A solution of 13 5 g. of potassium cyanide in 37 cc. of water was slowly dropped into a solution of 21 g. of benzal-*p*-chloroacetophenone in 300 cc. of alcohol and 5.6 g. of acetic acid. The mixture was stirred mechanically and kept at a temperature of 35–40° for eight hours during which all of the unsaturated ketone disappeared. The mixture was then chilled and filtered, the solid washed with water and alcohol and recrystallized from alcohol. The pure nitrile crystallizes in fine, white needles; m. p., 121°.

Anal. Calcd. for $C_{16}H_{12}ONCl$· C, 71.2; H, 4.5. Found: C, 71.0; H, 4.6.

Methyl α-Phenyl-β-[*p*-chlorobenzoyl]propionate.—As it usually is easier to change secondary nitriles into esters and hydrolyze these, than to go directly from nitrile to acid, the nitrile was suspended in twice its weight of absolute methyl alcohol, and the mixture saturated with dry hydrogen chloride. The nitrile dissolved and in the course of eight days the orange solution deposited nearly its own weight of methyl ester. This was recrystallized from methyl alcohol and thus obtained in colorless flakes; m. p., 111.5°.

Anal. Calcd. for $C_{17}H_{15}O_3Cl$: C, 67.4; H, 5.0. Found: C, 67.2; H, 5.1.

α-Phenyl-β-[*p*-chlorobenzoyl]propionic Acid, VIII.—The methyl ester was heated on a steam-bath with an excess of a 10% solution of potassium hydroxide in methyl alcohol until a sample of the solution remained clear when poured into water. The entire solution was then diluted with water and acidified. It deposited almost pure acid. This was recrystallized from methyl alcohol, forming colorless plates melting at 152°.

Anal. Calcd. for $C_{16}H_{13}O_3Cl$: C, 66.5; H, 4.5. Found. C, 66.3; H, 4.7.

α-Phenyl-β-bromo-β-[*p*-chlorobenzoyl]propionic Acid, IX.—The ketonic acid was brominated with the greatest ease. Thus when bromine was dropped slowly into a suspension of the acid in eight times its weight of boiling chloroform, the bromine disappeared at once, the acid dissolved gradually and the bromo acid crystallized from the solution immediately after all of the bromine had been added. It was washed and recrystallized from methyl alcohol; it gave long, colorless needles; m. p., 216°.

Anal Calcd. for $C_{16}H_{12}O_3BrCl$: C, 52.3; H, 3.3. Found: C, 52.1; H, 3 5.

Replacement of Bromine by Hydroxyl.—Ten g. of the bromo acid was dissolved in 100 cc. of 1% aqueous sodium hydroxide. The solution turned yellow and gradually became turbid. After 18 hours it was extracted with ether which removed 0 5 g. of benzal-*p*-chloro-acetophenone. The aqueous layer was acidified and the acid isolated in the usual manner. The crude acid melted at 115° but on recrystallization from an ether-petroleum ether mixture the melting point gradually rose to 139–140° and it remained the same after the acid had been mixed with the product obtained by hydrolyzing the oximido ester.

Formation of the Oximido Acid.—A solution of 0.5 g. of the ketolic acid in 10 cc. of 5% sodium hydroxide solution was treated with 5 g. of hydroxylamine hydrochloride, then warmed on a steam-bath for five minutes. The clear yellow solution was diluted with water, acidified and extracted with ether. On evaporation the ethereal solution deposited 0.35 g. of a substance that melted at 174°, and proved to be the same acid that had been obtained by hydrolysis of the oximido ester.

Esterification of the Oximido Acid.—A solution of the oximido acid in five times its weight of methyl alcohol was saturated with dry hydrogen chloride and set aside for three days. It was then evaporated under diminished pressure. The solid residue, after recrystallization from methyl alcohol, melted at 167°. Since this was also the melting point of a mixture of this synthetic product and the substance obtained by the action of potassium acetate on the bromoketone, the proof that the latter is the oximido ester (IV) is complete.

Esterification of the Ketolic Acid.—The oximido ester was also made by first esterifying the ketolic acid and then introducing the oximido group. For this purpose it was first shaken with an excess of saturated sodium carbonate solution which turned it into a sodium salt that separated in lustrous plates. The salt was washed with ice water, then dissolved in a large volume of water and changed into the silver salt by addition of silver nitrate. The vacuum-dried and finely powdered silver salt was boiled with methyl iodide in absolute ether. It gave an excellent yield of methyl ester.

Anal. Calcd. for $C_{17}H_{15}O_4Cl$: C, 64.0; H, 4.8. Found: C, 64.0; H, 4.7.

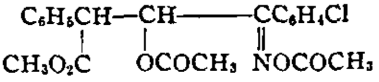
Methyl α-Phenyl-β-hydroxy-γ-oxo-γ-[*p*-chlorophenyl]butyrate.—The ketolic ester crystallizes in colorless plates and melts at 105°. Like the esters of most other ketolic acids it is hydrolyzed by bases with great rapidity. In order to turn it into the oximido ester it was necessary, therefore, to operate in a neutral solution. A mixture composed of 0 5 g. of the ester, 0.25 g. of hydroxylamine hydrochloride, 0.5 g. of precipitated calcium carbonate and 15 cc. of methyl alcohol was boiled for ten minutes, then cooled and filtered. From the filtrate, after dilution and acidification, ether extracted 0.5 g. of oximido ester—an excellent yield.

III. The Acyl Derivatives of the Oximido Ester

The oximido ester forms, in succession, a mono- and a diacetate. Both are easily hydrolyzed to the ester by methyl alcoholic hydrochloric acid. Both are also easily hydrolyzed by dilute aqueous ammonia, but the hydrolysis of the diacetate is only partial and the product is an isomeric monoacetate. Since the acyl derivatives of oximes are easily hydrolyzed as well as easily formed, the relation between the three acetates is represented by the following formulas.

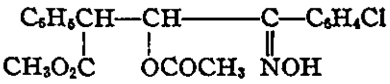
$$\mathrm{C_6H_5\underset{\underset{\displaystyle CH_3O_2C}{|}}{C}HCHOH\underset{\underset{\displaystyle NOCOCH_3}{\|}}{C}C_6H_4Cl}$$

X



$$\mathrm{C_6H_5\underset{\underset{\displaystyle CH_3O_2C}{|}}{C}H{-}\underset{\underset{\displaystyle OCOCH_3}{|}}{CH}{-\!-\!-}\underset{\underset{\displaystyle NOCOCH_3}{\|}}{C}C_6H_4Cl}$$

XI



$$\begin{array}{lll} C_6H_5CH- & CH- & C-C_6H_4Cl \\ \quad | & \;\, | & \;\, \| \\ CH_3O_2C & OCOCH_3 & NOH \end{array}$$

XII

The Mono-acetate, X.—When the finely powdered oximido ester was added to twice its weight of acetic anhydride, it dissolved and in a few minutes the solution contained nothing that was capable of forming a copper derivative. The solution was poured into twice its volume of 30% acetic acid, which dissolved it and rapidly destroyed the excess of anhydride, then diluted with water and extracted with ether. The extract was washed with sodium carbonate solution, dried, concentrated and diluted with petroleum ether. The acetate separated in small, colorless prisms which, after crystallization from an ether-petroleum ether mixture, melted at 105°.

Anal. Calcd. for $C_{19}H_{18}O_5NCl$: C, 60.7; H, 4.8. Found: C, 60.6; H, 5.0.

THE CORRESPONDING BENZOATE.—The corresponding benzoate was made by the Schotten-Baumann reaction and purified by recrystallization from acetone and ether; it gave stout needles; m. p., 134–135°.

Anal. Calcd. for $C_{24}H_{20}O_5NCl$: C, 65.8; H, 4.6. Found: C, 65.8; H, 4.9.

HYDROLYSIS OF THE ACETATE.—When a solution of the mono-acetate in methyl alcohol containing a little hydrochloric acid was tested at intervals with copper acetate it soon gave the characteristic copper derivative of the oximido ester. After 48 hours the test was negative. Ether then extracted the ketolic ester in almost the calculated quantity.

α-Phenyl-β-hydroxy-γ-oximido-γ-[*p*-chlorophenyl]butyramide, $C_6H_5CH(CONH)_2$-$CHOHC(NOH)C_6H_4Cl$.—When an ethereal solution of the mono-acetate or of the oximido ester itself is shaken with 6 *N* aqueous ammonia, it gradually deposits the amide in long, fine needles. After recrystallization from acetone, from which it separates in clumps of stout needles, the amide melts at 171°. Like the oximido ester it forms an insoluble copper derivative.

Anal. Calcd. for $C_{18}H_{17}O_4N_2Cl$: C, 60.5; H, 4.8. Found: C, 60.1; H, 4.6.

Acetate of the Ketolic Ester, $C_6H_5CH(CO_2CH_3)CH(OCOCH_3)COC_6H_4Cl$.—In order to compare the relative ease with which the hydroxyl and oximido groups are acetylated we also subjected the ketolic ester to the action of acetic anhydride. We found that the acetylation of the ketolic ester is much more difficult than that of the oximido ester. The acetate can be made by boiling the ester with five times its weight of acetic anhydride for 30 minutes and then evaporating the excess of anhydride in a vacuum. By recrystallization from an ether-petroleum ether mixture the acetate was obtained in colorless needles; m. p., 84–85°.

Anal. Calcd. for $C_{19}H_{18}O_5Cl$: C, 63.2; H, 4.7. Found: C, 62.8; H, 4.9.

THE DIACETATE, XI.—The diacetate is most easily made by dissolving the oximido ester or either of its mono-acetyl derivatives in five times its weight of acetyl chloride and allowing the solution to evaporate slowly. No other product is formed. The substance is sparingly soluble in ether, readily soluble in methyl alcohol and in acetone and crystallizes in large, colorless plates; m. p., 122°.

Anal. Calcd. for $C_{21}H_{20}O_6NCl$: C, 60.4; H, 4.9; Cl, 8.5. Found: C, 60.4; H, 5.0; Cl, 8.6.

HYDROLYSIS TO THE MONO-ACETATE, XII.—With methyl alcoholic hydrochloric acid the diacetate behaves exactly like the mono-acetate, but with aqueous ammonia its behavior is different. A saturated ethereal solution was shaken for 24 hours with a large excess of 6 *N* ammonium hydroxide. The ethereal layer was washed until free from ammonia, dried, concentrated and mixed with petroleum ether. This precipitated a fine powder which changed to large, colorless needles when recrystallized slowly from ether-petroleum ether; m. p., 151°.

Anal. Calcd. for $C_{19}H_{18}O_5NCl$: C, 60.7; H, 4.8. Found: C, 61.1; H, 5.1.

Benzoylation, $C_6H_5CH(CO_2CH_3)CH(OCOCH_3)C(NOCOC_6H_5)C_6H_4Cl$.—A solution of 1 g. of the second mono-acetate in 10 cc. of ether was shaken with an equal weight of benzoyl chloride and 8 cc. of 8% sodium carbonate solution for two hours. The ethereal layer yielded a powdery solid; m. p., 128°.

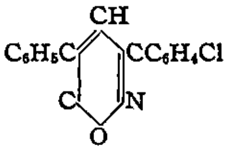
Anal. Calcd. for $C_{26}H_{22}O_6NCl$: C, 65.6; H, 4.6. Found: C, 66.3; H, 4.8.

THE DIBENZOATE.—Although benzoylation by the Schotten-Baumann method stops with the introduction of one benzoyl group, it is possible to make a dibenzoate of the oximido ester by using pyridine. Thus, when a solution of 1 g. of the ester and 4 g. of benzoyl chloride in 10 g. of pyridine was warmed on a steam-bath for 30 minutes and then manipulated in the usual manner, it gave 1 g. of the dibenzoate. This crystallized from methyl alcohol in needles. The melting point, 135°, is the same as that of the monobenzoate, but a mixture of the two melts much lower.

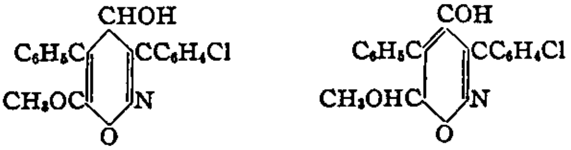
Anal. Calcd. for $C_{31}H_{24}O_6NCl$: C, 68 7; H, 4.5. Found: C, 68.7; H, 4.7.

IV. The Oxazine Derivatives

Two *o*-oxazine derivatives appeared in the course of the investigation. One of these (XIII) is formed as a by-product in the reaction between potassium acetate and the bromonitroketone. It crystallizes slowly from the oils left after removal of the cyclopropane derivatives and the oximido esters. It is completely insensitive to acids and but little affected by dilute bases, but forms a water-soluble sodium compound when digested with sodium alcoholate or concd. sodium hydroxide solution. The formula is based mainly on its relation to an analogous diphenyl compound for which the *o*-oxazine formula has been established by synthesis.



XIII



XIV

The second *o*-oxazine derivative is formed by the action of dimethyl sulfate and dilute alkali on the oximido ester. The structure is not quite certain, but it is difficult to find any other formula with which to represent a substance that has this composition, forms a benzoyl derivative and is changed to the oximido acid by bases, to the ketolic ester by acids.

5-Phenyl-3-[*p*-chlorophenyl]-6-oxo-orthoxazine, XIII.—The substance crystallizes in flat needles melting at 164°. It is very soluble in methyl alcohol and in chloroform and readily soluble in acetone. It very readily reduces permanganate both in water and in acetone. Sodium alcoholate converts it into a solid sodium compound which is insoluble in alcohol, soluble in water, and which reverts to the orthoxazine when acidified.

Anal. Calcd. for $C_{16}H_{10}O_2NCl$: C, 67.7; H, 3.5. Found: C, 67.4; H, 3.5.

5-Phenyl-3-[*p*-chlorophenyl]-4-hydroxy-6-methoxy-orthoxazine, XIV.—To a boiling solution containing 5 g. of the oximido ester and 5 g. of dimethyl sulfate in 10 cc. of ether, 40 cc. of 10% aqueous sodium hydroxide was added drop by drop. A crystalline solid appeared in the ethereal layer. After boiling the mixture for 20 minutes, this solid was removed, washed, dried and purified by repeated recrystallization from methyl alcohol; it gave thin plates melting at 184°. The yield was 2.5 g. and the only other product was the oximido acid which was isolated by acidifying the alkaline solution and extracting with ether.

Anal. Calcd. for $C_{17}H_{14}O_3NCl$: C, 64.7; H, 4.5. Found: C, 64.0; H, 4.8.

A molecular-weight determination in methyl alcohol gave 343 instead of 313 as calculated and a methoxyl determination by the Zeisel method showed the presence of one methoxyl group.

BENZOYLATION.—Using pyridine as the condensing agent, benzoylation resulted in a solid product which crystallized from acetone in large clumps of needles; m. p., 215–216°.

Anal. Calcd. for $C_{24}H_{18}O_4NCl$: C, 68.6; H, 4.3. Found: C, 68.3; H, 4.7.

HYDROLYSIS.—A solution of 1 g. of the oxyazine in 10 cc. of a 1% solution of sodium methylate was boiled for 30 minutes, then diluted, acidified and extracted with ether. The ethereal solution yielded about 0.5 g. of the oximido acid. A solution of the same substance in 10 cc. of methyl alcohol to which 3 cc. of concd. hydrochloric acid had been added was set aside for 48 hours, then evaporated under diminished pressure. It gradually deposited about 0.5 g. of the ketolic ester.

Summary

1. An α-bromo-γ-nitroketone, when treated with methyl alcoholic potassium acetate, gave four products: two isomeric cyclopropane derivatives, an oximido-hydroxy ester, and an oxyazine derivative. There are good reasons for believing that this represents the general behavior of those α-bromo-γ-nitroketones that have no other substituents in the γ position.

2. The oximido-hydroxy ester, the corresponding acid and the ketolic acid were synthesized in a different manner. They contain three reactive groups, are sensitive both to acids and bases and undergo a great variety of reactions.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE POLARIMETRY SECTION, BUREAU OF STANDARDS, UNITED STATES DEPARTMENT OF COMMERCE][1]

RELATIONS BETWEEN ROTATORY POWER AND STRUCTURE IN THE SUGAR GROUP. XVII.[2] THE STRUCTURE OF NEOLACTOSE

BY ALFONS KUNZ AND C. S. HUDSON

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When the conversion of lactose octa-acetate by active aluminum chloride to the chloro-acetyl derivative of another disaccharide, neolactose, was observed[3] it was thought that neolactose might be identical with Bergmann's 5-galactosido-mannose[4] since epimerizations at Carbon 2 are often met in sugar reactions. Experiment soon showed, however, that neolactose is a new sugar. The phenylosazone of neolactose proved to be very different from the easily recognized lactose osazone, a substance that is also the osazone of 5-galactosido-mannose, just as glucose and mannose give glucose osazone. Neolactose was obtained as a sirup by the de-acetylation of its octa-acetate and its aqueous solution was dextrorotatory, but after hydrolysis of the sugar with hydrochloric acid the products were levorotatory. This sharply distinguishes neolactose from 5-galactosido-mannose, both the component hexoses of which are dextrorotatory. It thus became evident that the structural change in the lactose molecule which results from the action of aluminum chloride upon lactose octa-acetate is not a simple epimerization at Carbon 2, as first suspected, and accordingly a detailed study of the nature of the component hexoses of neolactose was undertaken. Oxidation of the sugar by nitric acid yielded mucic acid in about the same proportion that is obtainable from lactose, which showed that one of the hexoses is a galactose, though whether it is *d*- or *l*-galactose was not evident because both forms yield mucic acid. Neolactose was then oxidized by bromine to its monobasic neolactobionic acid, which was obtained as a sirup free from substances that reduce Fehling's solution. Its hydrolysis by hydrochloric acid gave a good yield of a crystalline hexose which was readily identified as *d*-galactose, and an hexonic acid which gave

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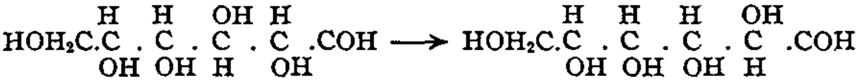
[1] Published by permission of the Director of the Bureau of Standards.

[2] Article XVI was published in THIS JOURNAL, 48, 2002 (1926). Occasion is here taken to correct an error in Article XIII [THIS JOURNAL, 48, 1434 (1926)], where it was stated that Irvine and Burt had observed a rearrangement of tetramethyl-γ-methyl-mannoside to tetra-methyl-α-methyl mannoside. Their observation was, however, that γ-methyl-mannoside readily rearranges to α-methyl-mannoside, a change which appears to consist, as they state, in a shifting of the oxygen ring while the reducing group remains substituted. A shifting of a methyl group does not take place in this change. In Article XIV [THIS JOURNAL, 48, 1437 (1926)], $-y$ was misprinted for $+y$ in the line above Table II and y for Y in Equation 8.

[3] Kunz and Hudson, *ibid.*, 48, 1978 (1926).

[4] Bergmann, *Ann.*, 434, 79 (1923).

a crystalline brucine salt that showed the melting point and rotation that Levene and Meyer[5] have observed for brucine *d*-altronate. The melting point of the brucine salt was not affected by mixing the substance with a specimen of Levene and Meyer's original preparation and it became almost certain, therefore, that the second hexose component of neolactose is *d*-altrose. Conclusive proof that such is the case was then obtained by hydrolyzing neolactose, obtaining crystalline *d*-galactose in good yield and an accompanying sirupy sugar which yielded crystalline *d*-altrose phenylosazone and, on oxidation with nitric acid, gave crystalline *d*-talomucic acid. The structure of neolactose is thus *d*-galactosido-*d*-altrose and its *d*-altrose component owes its origin to the action of aluminum chloride upon the acetylated structure of *d*-glucose which is present in the molecule of lactose octa-acetate or chloro-hepta-acetate. This is a new type of isomerization in the sugar group and a remarkable stereochemical change, since both Carbon atoms 2 and 3 of the glucose structure are isomerized.



$$\mathrm{HOH_2C.}\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}\,.\,\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}\,.\,\overset{\mathrm{OH}}{\underset{\mathrm{H}}{\mathrm{C}}}\,.\,\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}\,\mathrm{.COH} \longrightarrow \mathrm{HOH_2C.}\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}\,.\,\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}\,.\,\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}\,.\,\overset{\mathrm{OH}}{\underset{\mathrm{H}}{\mathrm{C}}}\,\mathrm{.COH}$$

d-glucose *d*-altrose

Having in hand a sufficient supply of a crystalline derivative of *d*-altrose (that is, α-neolactose octa-acetate) from which this hexose could be obtained by the reactions of de-acetylation and acid hydrolysis, which run smoothly and nearly quantitatively, it was sought to learn the rotation, hitherto unmeasured, of this very rare hexose. It was found that the equimolecular mixture of *d*-galactose and *d*-altrose that results from the acid hydrolysis of neolactose shows $[\alpha]_D = -8.95$ in water, from which it follows, since *d*-galactose shows $[\alpha]_D = +80$, that the $[\alpha]_D$ value of *d*-altrose is approximately -98 in water. It is evidently a very strongly levorotatory sugar and of about the same rotation as *d*-arabinose ($[\alpha]_D^{20} = -105$, final), a pentose of closely similar configuration. In like manner, the $[\alpha]_D$ value of neolactose has been found to be approximately $+ 35°$ in water.

Thanks are expressed to Dr. P. A. Levene for supplying the specimen of brucine *d*-altronate. One of the authors (A. K.) expresses his thanks to the International Education Board for a grant that enabled him to take part in this research.

Experimental Part

Phenylhydrazine Derivative of Neolactose.—Two g. of α-neolactose octa-acetate was de-acetylated by mixing the solution in 50 cc. of absolute chloroform with 33 cc. of absolute methyl alcohol in which 0.33 g. of metallic sodium had been dissolved.[6] Both solutions were previously cooled in an ice- and salt-bath and the mixture was kept therein for one-half hour. Five cc. of ice water was then added and after a further hour's standing the solution was made slightly acid with acetic acid and evaporated under re-

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[5] Levene and Meyer, *J. Biol. Chem.*, **26**, 363 (1916).

[6] Zemplén, *Ber.*, **59**, 1254 (1926). Zemplén and Kunz, *Ber.*, **56**, 1705 (1923).

duced pressure to a sirup which was dissolved in 30 cc. of water containing 1.5 g. of phenylhydrazine hydrochloride. The mixture was heated on the steam-bath one hour and a half, and as it cooled small, rather dark colored crystals separated which were recrystallized from 30 cc. of hot water; yield, 0.3 g. The substance, which is presumably neolactose phenylosazone, consists of yellow crystals that melt at 195° with decomposition. It is more soluble in water than lactose phenylosazone and does not form an insoluble anhydride derivative, as does the latter, when heated with dil. sulfuric acid. Certainly, neolactose does not yield lactose phenylosazone and therefore cannot be Bergmann's 5-galactosido-mannose.

Neolactobionic Acid.—Fischer and Meyer's directions[7] for preparing lactobionic and maltobionic acids have been followed. Forty g. of α-neolactose octa-acetate was de-acetylated in the manner already described and the resulting neolactose sirup was dissolved in 150 cc. of water and allowed to react with 20 g. of bromine for two days at room temperature. The excess of bromine was removed by a stream of air, the hydrobromic acid by silver carbonate and the excess of silver by hydrogen sulfide and the solution was concentrated under reduced pressure to 50 cc. To 45 cc. of this solution, a filtered hot solution of basic lead acetate was added until no further precipitate formed. The amorphous precipitate was filtered off, washed with water, alcohol and ether and dried. The weight was 52 g. This lead salt was decomposed with hydrogen sulfide, the filtered solution evaporated under reduced pressure to dryness, the residue dissolved in hot alcohol and then poured into absolute ether. The clear ether was decanted from the viscous sirup which was then dissolved in hot alcohol and evaporated to dryness under reduced pressure. This operation was repeated and lastly the evaporation was made with absolute ether. The yield was 6 g. of almost colorless sirup that did not reduce Fehling's solution. Neolactobionic acid closely resembles lactobionic and maltobionic acids. Like them it is amorphous and no crystalline salt of it has so far been obtained.

Hydrolysis of Neolactobionic Acid.—A solution of 6 g. of neolactobionic acid in 30 cc. of 5% sulfuric acid was heated on the steam-bath for one hour, neutralized with barium carbonate, filtered and the filtrate evaporated under reduced pressure to a sirup, which was dissolved in a small amount of water and poured into hot absolute alcohol. The barium salt that precipitated was subjected again to the same operation, after which it was found to be free from reducing sugars by the Fehling test. The two alcoholic solutions were united and evaporated under reduced pressure to dryness and this residue was dissolved in a small volume of hot methyl alcohol, from which solution a sugar readily crystallized. Its rotation ($[\alpha]^{22}_{D}$ = +80.7, final, in water) and its conversion to mucic acid showed it to be *d*-galactose. The sugar-free barium salt mentioned above was found to reduce Fehling's solution after heating with acid, which indicated that it contained some barium neolactobionate due to incomplete hydrolysis. A solution of 3 g. of it in 25 cc. of 5% sulfuric acid was accordingly heated on the steam-bath for two hours and then neutralized with barium carbonate and the barium salt separated from sugar as already described. The yield was 2.2 g. of barium salt and a second portion of crystalline *d*-galactose.

Two g. of the barium salt was dissolved in water, the barium was removed quantitatively as sulfate and the filtrate was evaporated under reduced pressure to a sirup which was dissolved in a little methyl alcohol and the solution poured into 50 cc. of ethyl acetate to precipitate impurities. The filtered solution was then evaporated to a thick sirup; yield, 0.8 g. This material did not reduce Fehling's solution. It was decidedly dextrorotatory; a solution of it in 10 cc. of water in a 1-dcm. tube rotated the sodium ray 1.36° to the right. This solution was heated on the steam-bath with 2 g. of brucine

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[7] Fischer and Meyer, *Ber.*, *22*, *361*, *1941* (*1889*).

for one-half hour, the excess of brucine was extracted with chloroform and the solution evaporated to dryness. The residue crystallized readily from alcohol. After three recrystallizations the substance showed $[\alpha]_D = +23.7$ in water; m. p., 158°, with decomposition. These are characteristic properties of brucine *d*-altronate[5] and, through the kindness of Dr. Levene, a mixed-melting-point measurement was made by the use of some brucine *d*-altronate that had been prepared from *d*-altronic acid obtained from *d*-ribose;[8] the melting point was the same, 158°.

The Hydrolysis of Neolactose.—A solution of 20 g. of α-chloro-acetyl neolactose in 200 cc. of acetone and 10 cc. of water was refluxed for two hours with 10 g. of freshly prepared silver carbonate, the silver chloride and excess of carbonate were filtered off and the filtrate was evaporated to dryness under reduced pressure. The residue was hydrolyzed by heating it at 98° with 200 cc. of *N* hydrochloric acid for two and one-half hours. The hydrochloric acid was removed with silver carbonate, the excess of silver with hydrogen sulfide, and the solution evaporated under reduced pressure to a thick sirup. The solution of this in 30 cc. of methyl alcohol and the addition of 15 cc. of ether resulted in a rapid crystallization of *d*-galactose which was complete in 24 hours in the ice box. The yield was 4.3 g. and 4.5 g., respectively, in two experiments. After one recrystallization from alcohol, the sugar showed $[\alpha]^{25}_D = +80.1$, and 2 g. of it yielded 2.15 g. of *d*-galactose phenylosazone, which was purified by two recrystallizations from 50% alcohol and one from absolute alcohol. The pure osazone melted with decomposition at 195° and gave the initial (+0.77) and final (+0.32) rotations in a mixture of six volumes of 95% alcohol and four volumes of pyridine (1-dcm. tube, 1 g. of osazone per 100 cc. of solvent, sodium light) that are characteristic of the osazone of galactose.[9] The other hexose that results from the hydrolysis of neolactose was identified as *d*-altrose by its conversion to *d*-altrose phenylosazone and its oxidation to *d*-talomucic acid, as follows.

d-**Altrose Phenylosazone.**—The sirupy mixture of *d*-altrose and *d*-galactose which was obtained as the mother liquor from a crystallization of *d*-galactose (4.5 g.), as described above, was dissolved in 100 cc. of a solution containing 12 cc. of pure phenylhydrazine in 12 cc. of 50% acetic acid and the mixture heated for three hours at 98°. The hot solution was decanted from the precipitated solids and oil and filtered while still warm; Fraction A (0.2 g.) separated therefrom. The solids and oil were extracted with 800 cc. of hot water (80°), and from this solution, after filtration, Fraction B (1 g.) separated. A second extraction with 500 cc. of hot water (85°) yielded Fraction C (0.3 g.). The residue was dissolved in 50 cc. of 50% hot alcohol and, on cooling, Fraction D (0.6 g.) separated. Fraction B contained most of the *d*-altrose phenylosazone (initial rotation, −0.28; final, −0.24, expressed in the units mentioned previously in the measurement on galactose osazone). Fraction A was of about the same composition, Fraction C was dark colored and was discarded and Fraction D contained mostly *d*-galactose phenylosazone. Fraction B was extracted with cold ether, petroleum ether was added until the solution became slightly turbid and the filtered solution soon yielded crystals of *d*-altrose phenylosazone. After one recrystallization from ether and petroleum ether, the substance melted with decomposition at 168–170° and showed initial and final levorotations of −0.37 and −0.30, respectively. The melting point is somewhat lower than that which Levene and La Forge found (178°), but the rotations agree with their measurements.

d-**Talomucic Acid.**—Fischer's directions[10] for preparing this acid have been followed.

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[8] Levene and Jacobs, *Ber.*, **43**, 3141 (1910).

[9] Neuberg, *Ber.*, **32**, 3386 (1900). Levene and La Forge, *J. Biol. Chem.*, **20**, 429 (1915).

[10] Fischer, *Ber.*, **24**, 3622 (1891).

The mother liquor after the crystallization of galactose (4.3 g.) following the acid hydrolysis of neolactose (see under that heading) was evaporated under reduced pressure to a sirup and this was oxidized with 40 cc. of nitric acid (d., 1.15) by evaporation to dryness on the steam-bath during constant stirring, adding water and evaporating again. The solution of the residue in 50 cc. of cold water slowly deposited about 0.1 g. of mucic acid. The filtrate therefrom was diluted to 75 cc., heated for two hours on the steam-bath with calcium carbonate in excess, purified with active carbon, and from the filtered hot solution a calcium salt crystallized as a yellow powder. The mother liquor from this was concentrated to 50 cc. and heated with calcium hydroxide and, on filtering and cooling, a second crop of calcium salt was obtained. Further crops were produced similarly and the total yield was 3 g. of crude calcium salt. This was added gradually to 50 cc. of a hot aqueous solution containing 1.6 g. of oxalic acid, the solution treated with decolorizing carbon, the excess of oxalic acid quantitatively precipitated with lime water, and the filtrate concentrated under reduced pressure to a sirup. The extraction of this residue with acetone left behind about 0.3 g. of mucic acid. The acetone solution of *d*-talomucic acid was evaporated to a sirup from which 1.2 g. of pure calcium *d*-talomucate was obtained by the procedure already described. Its calcium content was found to be 15.93% (0.1223 g. of salt, dried at 105°, yielded 0.0662 g. of calcium sulfate) while that calculated is 16.13%. One g. of the pure calcium salt was quantitatively decomposed by oxalic acid and, by Fischer's acetone extraction procedure, 0.2 g. of pure, crystalline *d*-talomucic acid was obtained; m. p., 158°; $[\alpha]_D^{22} = +29.2$ (initial), +24 (after one day) and +19 (after three days). These data agree well with Fischer's observations on *d*-talomucic acid.

The Approximate Rotation of Neolactose in Water.—By the de-acetylation of recrystallized α-neolactose octa-acetate according to the directions already given, the free sugar was obtained in sirupy form, and in aqueous solution it showed dextrorotation, $[\alpha]_D^{24} = +34.7$ (sugar from 1.099 g. of octa-acetate, 50 cc. of aqueous solution, 6-dcm. tube, 2.125 rotation). Under the same conditions pure lactose octa-acetate gave the value $[\alpha]_D^{24} = +54.4$ for its parent sugar (correct value for lactose, +55), which proves that the method is reliable. The equilibrium rotation of neolactose in water appears, therefore, to be approximately $[\alpha]_D = +35$.

The Approximate Rotation of *d*-Altrose in Water.—Some sirupy neolactose that was obtained by the de-acetylation of twice-recrystallized α-neolactose octa-acetate, as above described, was heated for two and one-half hours at 98° with 20 cc. of *N* hydrochloric acid and the cooled solution was made up to 50 cc. with water. The mixture of *d*-galactose and *d*-talose contained therein showed levorotation; $[\alpha]_D^{24} = -8.95$ (sugars from 1.0551 g. of octa-acetate, 50 cc. of solution, 6-dcm. tube, −0.601° rotation). Correcting for the equilibrium rotation of the galactose (+80) that of *d*-altrose is found to be approximately $[\alpha]_D = -98$. Evidently, this hexose is very strongly levorotatory, even more so than is *d*-fructose. The observed value is near that of *d*-arabinose (−105°, equilibrium) which is closely similar in configuration to *d*-altrose.

Summary

It is shown that the component hexoses of neolactose are *d*-galactose and *d*-altrose and that the new disaccharide is a *d*-galactosido-*d*-altrose. Neolactose results from a stereochemical rearrangement of the glucose portion of lactose (*d*-galactosido-*d*-glucose) brought about by the action of aluminum chloride upon lactose octa-acetate. This rearrangement is a new type of isomerization in the sugar group.

WASHINGTON, D. C.

[Contribution from the Chemical Laboratory, Case School of Applied Science]

THE INTERACTION OF ISOCYANIC ACID AND ISOCYANATES WITH SOME ALKYL AND ARYL SCHIFF BASES AND WITH HYDRAZONES. ADDITION TO THE CH:N LINKAGE

By N. A. Lange

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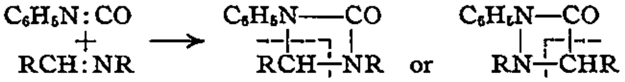
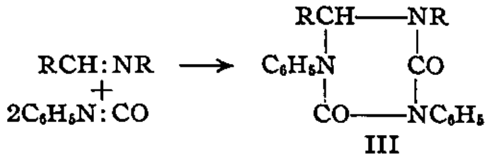
In previous communications[1] it has been shown that the addition of two molecular proportions of isocyanic acid to a Schiff base, where the alkyl groups ethyl, propyl, butyl and amyl are attached to the nitrogen atom of the C:N complex, resulted in the formation of a diketocyanidine. This reaction is analogous to the polymerization of cyanic acid to cyanuric acid and to the addition of two molecular proportions of a ketene to one of Schiff base.[2] As a continuation of this reaction, a further study has been made of the addition of phenylisocyanate to the same Schiff bases. The theoretical possibilities for such a condensation are few; reaction between the hydrogen attached to the carbon atom of the Schiff base and the oxygen atom of the isocyanate would be most unlikely, thus leaving direct addition at the double linkage between the carbon and the nitrogen atoms of the Schiff base as the expected point of attack. Equimolecular additions would then give 4-membered rings of two possible structures.



I II

The result could be distinguished easily, since such 4-membered rings are readily hydrolyzed as indicated by the dotted lines, I giving C_6H_5NHCO-NHR and RCHO while II would yield $RNH.N(C_6H_5)CHO$ and RCHO. Additions of two molecular proportions of isocyanate for one of Schiff base would give 6-membered rings containing three nitrogen atoms.



III

A 6-membered ring of this type would be expected to show the stability of cyanuric acid and, having no free amino or imino hydrogen, should not acetylate. The results of the experiments show that phenylisocyanate reacts with N-alkyl Schiff bases in the same manner as isocyanic acid, giving 6-membered diketocyanidines (III) which are stable, crystalline compounds, not affected by conditions likely to produce hydrolysis and not affected by acetylating agents. As compared with isocyanic acid, however, phenylisocyanate is not so reactive; whereas with the former,

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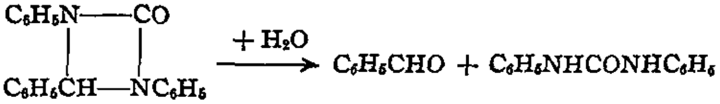
[1] Hale and Lange, This Journal, 41, 379 (1919); 42, 107 (1920).

[2] Staudinger, *Ann.*, 374, 11 (1911); *Ber.*, 50, 1042 (1917).

reaction takes place below room temperature, with the latter it is necessary to use temperatures above 150°; moreover, with phenylisocyanate the butyl and *iso*-amyl derivatives were never obtained in the many experiments under various conditions of time and temperature. Attempts to prepare the methyl derivatives from benzylidene-methylamine by the action of isocyanic acid in cold glacial acetic acid solution or by the action of phenylisocyanate at elevated temperatures were not successful. Molecular-weight determinations of the phenylisocyanate-benzylidene-ethylamine addition compound show conclusively that the compound is monomolecular.

All attempts to obtain addition compounds with phenylisocyanate and N-aryl Schiff bases were unsuccessful. Experiments with benzylidene-aniline or benzylidene-*p*-toluidine using one or two molecular proportions of phenylisocyanate for one of Schiff base gave results showing 6-membered rings are not produced. The reaction products had a decided odor of phenylisocyanate and when steam distilled gave the corresponding *sym.-disubstituted ureas, the formation*[3] *of which can be accounted for by* 4-membered ring formation or by hydrolysis of unchanged Schiff base and subsequent reaction of the liberated amine with the unchanged isocyanate.



$$\begin{array}{ll} C_6H_5N\text{---}CO & \\ \quad| \qquad\quad | & \xrightarrow{+H_2O} C_6H_5CHO + C_6H_5NHCONHC_6H_5 \\ C_6H_5CH\text{---}NC_6H_5 & \end{array}$$

or

$$(1)\quad C_6H_5CH{:}NC_6H_5 + H_2O \longrightarrow C_6H_5CHO + C_6H_5NH_2$$

$$(2)\quad C_6H_5NH_2 + C_6H_5NCO \longrightarrow C_6H_5NHCONHC_6H_5$$

Similar results were obtained in the interaction of isocyanic acid with N-aryl Schiff bases in glacial acetic acid, although in these cases the ureas condensed further with the aldehyde set free, giving white, highly insoluble ureides which probably are polymerized forms of the simple compound $C_6H_5CH(NHCONHR)_2$. These same insoluble ureides were obtained by direct condensation of the aldehyde and the substituted urea.

Attempts were made to bring about the addition of phenylisocyanate to the CH:N group in benzylidene and ethylidene *asym.*-diphenylhydrazones, compounds having no imino hydrogen. Numerous experiments under various conditions failed to bring about the addition; this failure to add to the CH:N group of phenylhydrazones finds its counterpart in the chemistry of the ketenes where such attempted additions met with failure.[4] Previous work of others has shown that hydrazones having imino hydrogen do add isocyanates. Benzylidene-phenylhydrazone is reported as adding phenylisocyanate to the imino nitrogen when warmed to 170° forming 1-benzylidene-2,4-diphenylsemicarbazone; likewise, benzylidene-benzylhydrazone with isocyanic acid gives 1-benzylidene-2-benzylsemicarbazone.[5]

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[3] Senier and Shepheard, *J. Chem. Soc.*, **95**, 504 (1909).

[4] Staudinger, "Die Ketene," F. Enke, Stuttgart, **1912**, p. 71.

[5] Busch and Walter, *Ber.*, **36**, 1360 (1903).

Experimental Part

The Schiff bases employed in this investigation were prepared by adding an equimolecular quantity of freshly distilled benzaldehyde to the amine in question (ethyl, propyl, phenyl, etc.), at 5–10°, extracting the solution with ether, washing with water and drying the ether solution over anhydrous potassium carbonate. After evaporation of the ether, the Schiff base remaining was distilled, if a liquid or, if a solid, recrystallized from alcohol.

1-Ethyl-3,5,6-triphenyl-2,4-diketo-hexahydrocyanidine, $C_2H_5.C_3HO_2N_3(C_6H_5)_3$.—A mixture of two molecular proportions of phenylisocyanate and one of benzylidene-ethylamine was sealed in a glass tube and heated to 180–200° for about four days; after the tube had cooled it was opened. The viscous reaction product was treated in the tube with an equal volume of alcohol and a few drops of ether. The crystals which usually separated after a short time were filtered off, washed with ether and recrystallized from alcohol. If no separation of crystals occurred after the addition of alcohol and ether to the original reaction mixture, overheating was indicated, in which case a low yield of the product could be obtained by steam-distilling the viscous material for several hours, decanting the water from the non-volatile residue and adding ether to this to remove the resinous impurities, leaving the insoluble crystalline cyanidine condensation product. It was found that the yield varied with the length of time of heating; the following yields of condensation product were obtained at 180–200°: after 48 hours, 21.4%; 72 hours, 36.6%; 96 hours, 39%; 120 hours, 29%; and after 168 hours at room temperature, 23.4%. The cyanidine is readily soluble in ethylene chlorohydrin or chloroform, fairly soluble in ethyl acetate, benzene, toluene, xylene, methyl alcohol, ethyl alcohol or amyl alcohol, slightly soluble in carbon tetrachloride and insoluble in water, ether or petroleum ether. It forms colorless crystals melting at 192° (corr.). When steam is passed through a suspension of the compound in hydrochloric acid or aqueous sodium hydroxide no hydrolysis occurs; the compound remains unchanged when boiled with acetic anhydride and fused sodium acetate. Molecular-weight determinations by depression of the freezing point were made with naphthalene as the solvent; the values obtained on 18 determinations of various concentrations gave a mean value of 380; the calculated value is 371.[6]

Anal. Calcd. for $C_{23}H_{21}O_2N_3$: C, 74.35; H, 5.70; N, 11.3. Found: C, 74.62; H, 5.74; N, 11.3.

1-Propyl-3,5,6-triphenyl-2,4-diketo-hexahydrocyanidine.—This compound was obtained in very poor yields by heating one molecular proportion of benzylidene-propylamine with two of phenylisocyanate in sealed tubes at 180–200°. Attempts to determine the optimum length of time of heating were unsuccessful, as in many cases tubes under supposedly identical conditions gave different yields varying from nothing to about 10% of the calculated amount. The values obtained on combustion were sufficient to identify it as the propyltriphenyldiketo-hexahydrocyanidine. It is fairly soluble in benzene, methyl alcohol, ethyl alcohol, carbon tetrachloride or acetone and insoluble in water, ether or petroleum ether. It forms colorless crystals from alcohol; m. p., 156° (corr.).

Anal. Calcd. for $C_{24}H_{23}O_2N_3$: C, 74.77; H, 6.02; N, 10.9. Found: C, 74.85; H, 6.01; N, 10.7.

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[6] The writer is indebted to Mr. Milton Zucker for these molecular-weight determinations.

1-Ethyl-6-phenyl-3,5-di(*p*-tolyl)-2,4-diketo-hexahydrocyanidine.—This compound was obtained in a 21% yield on heating one molecular proportion of benzylidene-ethylamine with two of *p*-tolylisocyanate in a sealed tube at 180–200° for 118 hours. After cooling, an equal volume of alcohol and a few drops of ether were added to the reaction mixture; after several hours, crystals of the condensation product separated; these were filtered off, washed with ether and recrystallized from alcohol. The substance formed colorless crystals which were fairly soluble in methyl alcohol, ethyl alcohol, carbon tetrachloride or acetone, slightly soluble in benzene and insoluble in water, ether or petroleum ether; m. p., 173° (corr.). It was not hydrolyzed on steam distillation in aqueous acid or alkaline suspensions and was not acetylated when boiled with acetic anhydride and fused sodium acetate.

Anal. Calcd. for $C_{25}H_{25}O_2N_3$: C, 75.15; H, 6.31; N, 10.5. Found: C, 74.62; H, 6.40; N, 10.2.

Benzylidene-bis-*p*-tolylureide; $[C_6H_5CH(NHCONHC_6H_4CH_3)_2]_x$.—A 1.2-g. yield of this ureide was obtained when 5 5 g. of benzylidene-*p*-toluidine in cold glacial acetic acid was treated with 4.6 g. of potassium cyanate and allowed to stand in the cold for 24 hours. The solid that separated was filtered off, washed successively with water, alcohol, hot acetone and then ether; the white powder thus obtained is insoluble in the common organic solvents; m. p., 206–208° (corr.).

Anal. Calcd. for $C_{23}H_{24}O_2N_4$: C, 71.10; H, 6.23; N, 14.4. Found: C, 71.16; H, 6.24; N, 14.3.

The same compound was obtained when two molecular proportions of *p*-tolyl urea and one of benzaldehyde in glacial acetic acid were warmed and then allowed to stand at room temperature; the white solid that separated was purified as described above.

Anal. Calcd. for $C_{23}H_{24}O_2N_4$: N, 14.4. Found: 14.8.

Both products hydrolyzed when steam-distilled in dil. hydrochloric acid, giving benzaldehyde and *p*-tolyl urea.

Benzylidene-bis-*o*-tolylureide, $[C_6H_5CH(NHCONHC_6H_4CH_3)_2]_x$.—This compound was obtained in a 1.8-g. yield from 6 g. of benzylidene-*o*-toluidine and 4 g. of potassium cyanate in acetic acid and was purified in the same manner as the *p*-toluidine isomer above. It formed a white powder insoluble in the common organic solvents; m. p., 199–200° (corr.).

Anal. Calcd. for $C_{23}H_{24}O_2N_4$: C, 71.10; H, 6.23; N, 14.4. Found: C, 71.29; H, 6.33; N, 13.8.

The same compound was obtained by the interaction of benzaldehyde with two molecular proportions of *o*-tolyl urea in glacial acetic acid.

Anal. Calcd. for $C_{23}H_{24}O_2N_4$: C, 71.10; H, 6.23; N, 14.4. Found: C, 70.92; H, 6.27; N, 14.1.

Both products, when steam-distilled in dil. hydrochloric acid, hydrolyzed forming benzaldehyde and *o*-tolyl urea.

Phenylisocyanate with Benzylidene-*p*-toluidine and with Benzylidene-aniline.—When benzylidene-*p*-toluidine and two molecular proportions of phenylisocyanate were heated in a sealed tube to 180–200° for 120 hours, a clear viscous liquid was obtained having a decided odor of phenylisocyanate. No crystals separated on standing nor were any obtained on treatment of the reaction mixture with various solvents. When steam distilled, benzaldehyde and *sym.*-*p*-tolylphenyl urea were obtained. When two molecular proportions of phenylisocyanate were heated with one of the same Schiff base the same results were obtained. Similar results were obtained when benzylidene-aniline replaced the benzylidene-toluidine; the products isolated from this reaction were correspondingly benzaldehyde and *sym.*-diphenyl urea.

Phenylisocyanate with α-Benzylidene-β,β-diphenylhydrazone and with α-Ethylidene-β,β-diphenylhydrazone.—Sealed tubes containing one molecular proportion of benzylidene-diphenylhydrazone with one of phenylisocyanate and with two of phenylisocyanate were heated for various periods of time at 180–200°. A light brown, viscous liquid was obtained which solidified to a transparent resin on cooling; benzylidenephenylhydrazone was the only crystalline material that could be obtained from a solution of this resin in alcohol. The mother liquors on evaporation left a resin from which no crystalline substances could be isolated either before or after steam-distillation. Ethylidene-diphenylhydrazone, when heated with one and with two molecular proportions of phenylisocyanate, similarly gave resinous products from which phenylcyanurate was the only crystalline product isolated.

Summary

Phenylisocyanate resembles the ketenes in the addition compounds that it forms with some alkyl Schiff bases, two molecular proportions adding to yield a 6-membered ring; aryl Schiff bases, on the other hand, do not give similar compounds, probably adding but one molecular proportion of the isocyanate to form unstable 4-membered rings which could not be isolated; attempts to add phenylisocyanate to the CH:N linking in hydrazones were not successful.

Cleveland, Ohio

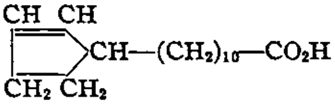
[Contribution from the Chemical Laboratory of the University of Illinois]

SYNTHESIS OF A HOMOLOG OF CHAULMOOGRIC ACID. Δ²-CYCLOPENTENYLACETIC ACID. VII

By C. R. Noller[1] with Roger Adams

Received June 24, 1926 Published September 4, 1926

The successful syntheses of dihydrohydnocarpic and dihydrochaulmoogric acids[2c] and many of their homologs[2g] has led us to determine whether a similar procedure might not be employed to obtain hydnocarpic acid (I) and chaulmoogric acid (II) and their homologs.



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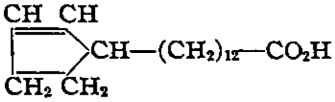

II

Although the preparation of hydnocarpic acid itself,[2a] the immediate goal, has not yet been reached, nevertheless a very important step forward has been made by finding a most satisfactory method for preparing certain Δ²-cyclopentenyl compounds which may be used as intermediates in syn-

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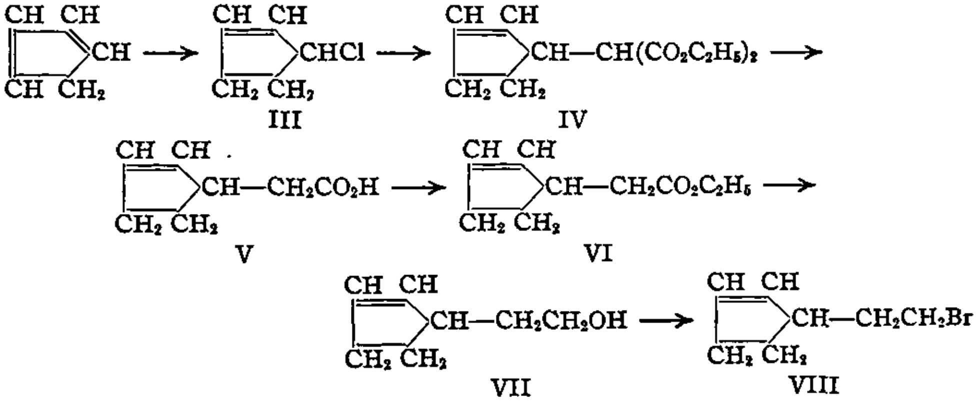
[1] This communication is an abstract of a portion of a thesis submitted by C. R. Noller in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

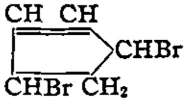
[2] (a) Shriner with Adams, This Journal, **47**, 2727 (1925). (b) Noller with Adams, *ibid.*, **48**, 1074; (c) 1080 (1926). (d) Hiers with Adams, *ibid.*, **48**, 1089 (1926). (e) VanDyke and Adams, *ibid.*, **48**, 2393 (1926). (f) Sacks with Adams, *ibid.*, **48**, 2395 (1926). (g) Hiers with Adams, *ibid.*, **48**, 2385 (1926).

theses in this field. This communication describes the preparation of *dl*-Δ^2-cyclopentenylacetic acid (V) and *dl*-β-(Δ^2-cyclopentenyl) ethanol (VII). The former is a *dl* homolog of the natural acids and the latter, after conversion to the corresponding bromide, may be made into the Grignard reagent and condensed according to the methods used by Noller and Adams[2b] and by Hiers and Adams[2d,2g] to obtain various acids containing the Δ^2-cyclopentenyl group. In fact, *dl*-methyl hydroxyhydnocarpate has already been prepared.

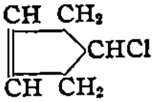
Cyclopentadiene adds dry hydrogen chloride 1–4, thus producing Δ^2-cyclopentenyl chloride[3] (III). This in turn may be condensed with malonic ester to give an excellent yield of Δ^2-cyclopentenyl-malonic ester (IV) which by saponification and decomposition gives Δ^2-cyclopentenyl acetic acid (VI). This Δ^2-cyclopentenylacetic acid is readily converted to the corresponding ester (VI) and reduced with sodium and alcohol to Δ^2-cyclopentenyl ethanol VII. The corresponding bromide (VIII) is being used for further syntheses.



Although no direct proof has been given in this investigation that the double bond in the cyclopentenyl chloride or the compounds derived from it is in the Δ^2 position, several facts leave little doubt that this conclusion is correct. In the first place Thiele[4] showed that bromine adds 1–4 to cyclopentadiene. He obtained two *cis-trans* isomeric dibromocyclo pentenes which on oxidation yielded, respectively, inactive and racemic α-γ-dibromoglutaric acid. Hence the original bromides must be Δ'-2,5-dibromocyclopentenes (IX).



IX



X

It seems logical to assume, therefore, that hydrogen chloride also adds 1–4.

Other evidence in favor of 1–4 addition is that if 1–2 addition had taken

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[3] Kraemer and Spilker, *Ber.*, **29**, 552 (1896). Noeldechen, *Ber.*, **33**, 3348 (1900).

[4] Thiele, *Ann.*, **314**, 301 (1901).

place, a mixture of two isomeric cyclopentenyl chlorides might be expected having Structures III and X, whereas 1–4 addition would yield only Compound III. In the preparation of the chloride and in subsequent reactions, excellent yields were obtained and there were no indications of more than a single product at any step.

Finally Δ^2-cyclopentenyl chloride should contain a very reactive halogen atom whereas in Δ^3-cyclopentenyl chloride (X) the halogen should be no more reactive than that in an ordinary secondary alkyl chloride. Actually it was found that the compound formed is very reactive. For example, it reacts practically quantitatively and rapidly with sodiomalonic ester in the cold, whereas ordinary alkyl chlorides usually require refluxing to bring about condensation. More rigorous proof of the structure of these compounds is now being attempted.

Mr. G. H. Coleman has kindly tested the sodium *dl*-Δ^2-cyclopentenyl acetate bacteriologically. He finds no bactericidal action toward *B. leprae.* Whether this ineffectiveness is due to the short side chain or to the lack of optical activity must be decided only after more compounds are available.

Experimental Part

Δ^2-Cyclopentenyl Chloride, III.—Dry hydrogen chloride was passed into 86 g. of freshly redistilled cyclopentadiene at a temperature of −20° to −15° until it was saturated. This operation required from one and one-half to two hours. The mixture was allowed to stand for two hours at a temperature of −15° to −5°. The crude product was then distilled under diminished pressure into a flask cooled to −20° to −15°. The total distillate amounted to 112–119 g. (84–89%); b. p., 25–31° at 30 mm. This compound is a colorless liquid and fairly stable when kept at −15°. At room temperature it rapidly decomposes. It was condensed with sodio-malonic ester immediately after distillation.

A sticky residue remained in the flask after distillation of the chloride, which in some respects resembled rubber. It was quite elastic and was soluble in benzene but insoluble in alcohol and in ether.

Δ^2-Cyclopentenylmalonic Ester, IV.—To 700 cc. of absolute alcohol placed in a three-neck flask fitted with a mechanical stirrer and efficient reflux condenser was added 29.9 g. (1.3 moles) of clean metallic sodium. After solution of the sodium in alcohol and cooling to 40–50°, 208 g. (1.3 moles) of redistilled malonic ester was slowly added. The solution was cooled as low as possible in an ice- and water-bath without causing the precipitation of the sodium salt (about 5°) and then 112 g. (1.1 moles) of cyclopentenyl chloride was added over a period of one hour. The mixture was allowed to stand overnight at room temperature and then refluxed for one and one-half hours during stirring. The product was worked up in the usual way and distilled under diminished pressure. A small low-boiling fraction of about 25 g. distilled first, followed by the main fraction of cyclopentenyl-malonic ester boiling over a range of 5°. The yield was 208–218 g. (84–88%). On redistillation, it boiled at 120° (corr.) at 6 mm.; n_D^{20}, 1.4536; d_4^{20}, 1.0507.

Anal. Subs., 0.2094: CO_2, 0.4860; H_2O, 0.1514. Calcd. for $C_{12}H_{18}O_4$: C, 63.69; H, 8.01. Found: C, 63.30; H, 8.03.

Δ^2-Cyclopentenylmalonic Acid.—A mixture of 113 g. (0.5 mole) of cyclopentenylmalonic ester and a solution of 60 g. of sodium hydroxide in 500 cc. of water was boiled until the ester was completely in solution, and then for two hours longer. The solution was evaporated over a free flame until the salt began to crystallize, cooled and acidified with concd. hydrochloric acid to the Congo red end-point, and extracted with ether until no more malonic acid was obtained on evaporation of the solvent from a portion of the last extraction. As much of the ether as possible was distilled from a steam-bath and the residue taken up in hot benzene. All of the product dissolved at first but, on boiling, the remaining ether was removed and the cyclopentenylmalonic acid separated. After cooling, the malonic acid was filtered with suction; yield, 83 g. (97.6%). Recrystallization from benzene gave colorless crystals; m. p., 149–149.5° (corr.), with loss of carbon dioxide.

Anal. Subs., 0.1326: CO_2, 0.2733; H_2O, 0.0717. Calcd. for $C_8H_{10}O_4$: C, 56.44; H, 5.94. Found: C, 56.21; H, 6.01.

Δ^2-Cyclopentenylacetic Acid, V.—In a 500cc. round-bottomed flask fitted with a reflux condenser was placed 127.5 g. (0.75 mole) of Δ^2-cyclopentenylmalonic acid. This was carefully heated in a metal bath to a temperature of 150–160°, when carbon dioxide began to be liberated. If the heating above the melting point is too rapid, the evolution of carbon dioxide is so great that some of the cyclopentenylacetic acid is carried out of the condenser. After complete liquefaction had taken place it was heated for one hour to a temperature of 190°. On vacuum distillation there was obtained 91–93 g. of Δ^2-cyclopentenylacetic acid; b. p., 95–100° at 4 mm. (96–99%). On redistillation, it boiled at 94–95° (corr.) at 3 mm.; n_D^{20}, 1.4682, d_4^{20}, 1.0519.

Anal. Subs., 0.1986: CO_2, 0.4823; H_2O, 0.1425. Calcd. for $C_7H_{10}O_2$: C, 66 61; H, 8.01. Found: C, 66.23; H, 7.97.

Ethyl Δ^2-cyclopentenylacetate, VI.—A solution of 87.5 g. (0.7 mole) of Δ^2-cyclopentenylacetic acid in 300 cc. of absolute ethyl alcohol containing nine drops of concd. sulfuric acid was refluxed for six hours. It was then treated with sufficient 40% potassium hydroxide solution to neutralize all of the sulfuric acid (alkaline to Congo red). The yield of a practically pure product boiling over a range of 3° was 87.5–89.5 g. (81–83%). On redistillation, the product boiled at 85–86° (corr.) at 15 mm.; n_D^{20}, 1.4480; d_4^{20}, 0.9659.

Anal. Subs., 0.2002: CO_2, 0.5110; H_2O, 0.1622. Calcd. for $C_9H_{14}O_2$: C, 70.08; H, 9.17. Found: C, 69.77; H, 9.00.

A portion of the cyclopentenylacetic acid was recovered from the sodium carbonate washings of the ether solution of the crude product by evaporation to a small volume and acidifying.

β-(Δ^2-Cyclopentenyl)Ethanol, VII.—To 15.4 g. (0.1 mole) of ethyl-Δ^2-cyclopentenylacetate placed in a three-neck flask fitted with a mechanical stirrer and an efficient reflux condenser was added 100 cc. of absolute ethyl alcohol. The solution was heated almost to boiling and then 10 g. of clean metallic sodium was added in small pieces during stirring, at first slowly and then more rapidly. The addition of sodium should be as rapid as possible without allowing the mixture to foam out of the flask and into the condenser. Stirring was continued until all of the sodium had reacted. About 60 cc. of water was added and the solution boiled for one-half hour. The alcohol was then distilled through a column until the temperature of the vapor reached 83°. About 200 cc. of water was added to the reaction mixture, and the upper layer was separated and washed twice with water. The aqueous layer and washings were extracted twice with ether and the ether extracts combined with the alcohol layer and dried over anhydrous magnesium sulfate. After the ether had been distilled from a steam cone, the residue was distilled under diminished pressure, when there was obtained 10 g. (89%)

of practically pure cyclopentenyl ethanol boiling over a range of 2°. On redistillation the alcohol boiled at 86–87° (corr.) at 16 mm.; n_D^{20}, 1.4721; d_4^{20}, 0.9446.

Anal. Subs., 0.1928: CO_2, 0.5259; H_2O, 0.1852. Calcd. for $C_9H_{12}O$: C, 74.93; H, 10.80. Found: C, 74.39; H, 10.70.

The yield of alcohol decreased slightly when larger quantities of ester were reduced, dropping to about 82% on a 0.5 mole run.

Summary

A process is described for preparing Δ^2-cyclopentenylacetic acid and β-(Δ^2-cyclopentenyl)ethanol. These substances are valuable intermediates for the syntheses of derivatives and homologs of hydnocarpic and chaulmoogric acids.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY, NEW YORK UNIVERSITY]

THE COMPOUND OF ORTHO-CRESOL AND PARA-CRESOL: A CORRECTION

BY ARTHUR E. HILL AND THOMAS W. DAVIS

RECEIVED JULY 2, 1926 PUBLISHED SEPTEMBER 4, 1926

In a recent paper on the cresols from this Laboratory,[1] evidence for the existence of a 1:1 compound was presented. Our attention has been directed to two earlier investigations of this system, by Fox and Barker[2] and by Dawson and Mountford;[3] the former found no evidence of compound formation and the latter found evidence of a compound of two molecules of the *p*-cresol with one of the *ortho*. We have repeated our investigation of the system by means of freezing-point determinations, and find that the conclusion of Dawson and Mountford is correct. Working with the greatest care to avoid undercooling and with the apparatus previously described[1] to insure absence of water, we have obtained the following data, which show a maximum for the freezing point of the compound lying near the

TABLE I

FREEZING POINTS OF *o*-CRESOL-*p*-CRESOL MIXTURES

o-Cresol, % by wt.	100	86.12	72.34	63.92	57.31	54.55	53.5[a]	52.11
F. p., °C.	30.80	24.61	14.71	8.25	3.02	1.13	0	1.81
Solid phase	*o*-	*o*-	*o*-	*o*-	*o*-	*o*-	*o* + comp.	comp.

o-Cresol, % by wt.	44.70	37.19	37.19[b]	35.13[b]	33.3[a]	32.36	20.10	9.66	0
F. p., °C.	6.62	7.84	5.13	7.19	8.1	10.10	21.25	29.19	34.61
Solid phase	comp.	comp.	*p*-	*p*-	comp. + *p*-	*p*-	*p*-	*p*-	*p*-

[a] By extrapolation.

[b] Metastable.

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[1] Hill and Mosbacher, THIS JOURNAL, **47**, 2544 (1925).

[2] Fox and Barker, *J. Soc. Chem. Ind.*, **18**, 268 (1918).

[3] Dawson and Mountford, *J. Chem. Soc.*, **113**, 923 (1918).

composition 2 *p*:1 *o*. Our earlier conclusion was probably in error because of failure to obtain equilibrium owing to the extreme viscosity of the cresols and their outstanding tendency to remain undercooled. The possibility that there exist both a 2:1 compound and a 1:1 is, of course, not excluded, but we have been unable to repeat the results showing the existence of the latter.

The eutectic between *o*-cresol and compound at 0° and the transition point of the compound to *p*-cresol at 8.1° were obtained by extrapolation; they are, respectively, 0.6 and 1.2° lower than found by Dawson and Mountford. The curves for the two components are in reasonable agreement with those of the same investigators.

New York, N. Y.

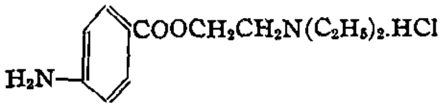
[Contribution from the Furman Chemical Laboratory of Vanderbilt University]

ESTERS OF THE PROCAINE TYPE DERIVED FROM NICOTINIC ACID

By A. W. Ingersoll and B. H. Robbins

Received July 2, 1926 Published September 4, 1926

The work reported in this paper was undertaken with a view to determine to what extent, if any, the local anesthetic properties of procaine (I) and its homologs would be retained in compounds of the same type derived from the pyridine-carboxylic acids. For this purpose the esters of nicotinic acid with β-diethylamino-ethyl alcohol (II) and with γ-diethylamino-propyl alcohol have been prepared and tested.



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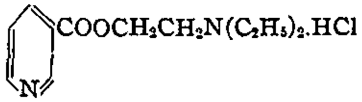

II

Of the pyridine-carboxylic acids, nicotinic acid is apparently the most closely related in structure to *p*-aminobenzoic acid, and was chosen for this reason.

Although several derivatives of partially hydrogenated nicotinic acid, notably arecoline,[1] are included among the potent alkaloids, few other derivatives of nicotinic acid have been studied as to their physiological behavior. Nicotinic acid itself is stated to be slightly poisonous and is detoxicated in dogs by conversion in part to the corresponding methylbetaine (trigonelline) and in part to nicotinyl glycine.[2] The diethyl- and dipropylamides and the piperidide have been patented as drugs.[3] While

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[1] S. Frankel, "Die Arzneimittel Synthese," J. Springer, Berlin, *1921*, pp. 41 and 311.

[2] Ackermann, *Z. Biol.*, **59,** 17 (1912).

[3] U. S. pat. 1,403,117 (1922).

the simple alkyl esters of nicotinic acid appear not to have been tested, the methyl ester methochloride (Cesol) is the representative of several analogs that have been patented as therapeutic agents.[4] No esters with amino alcohols have previously been described.

Previous studies on the relation of molecular structure to local anesthetic action in esters of the procaine type have shown, in general, that when the β-diethylamino-ethyl group is replaced by related groups, or when the *p*-aminobenzoyl group is replaced by other aromatic acyl groups, the resulting esters have at least some anesthetic activity. On the other hand, when the acyl groups are of the saturated aliphatic or mixed types, the resulting esters are but rarely anesthetics.[5] In fact, the existence of anesthetic action in compounds of this type, extending, as it does, to the esters of the thiophene-, furane- and pyrrole-carboxylic acids, has been proposed as a possible test for the "aromatic" nature of the acyl group involved.[5]

In view of the above considerations it was rather surprising to find, as the result of careful tests, that both of the esters prepared were entirely lacking in anesthetic properties. Also, no mydriatic action and only a slight toxicity were observed. Whether the absence of anesthetic action in these esters should be ascribed to an essentially non-aromatic character of the pyridine ring or to some other property peculiar to this ring cannot be decided at present. It is suggested that an examination of the esters derived from the isomeric pyridine-carboxylic acids would be interesting in this connection.

Discussion of the Syntheses

The esters, as monohydrochlorides, were prepared by the action of β-diethylamino-ethyl alcohol and γ-diethylaminopropyl alcohol, respectively, upon pure nicotinyl chloride in suspension in dry benzene or acetone. The nicotinyl chloride was prepared by heating nicotinic acid in a closed flask with a small excess of thionyl chloride dissolved in dry benzene. Meyer[6] has given general directions for preparing the chlorides of the pyridine-carboxylic acids by heating these in a sealed tube with a large excess of thionyl chloride as solvent. Attempts to apply his method to nicotinic acid invariably gave so large a proportion of the corresponding acid chloride-hydrochloride as to make this method unsatisfactory for our purpose. The modified method gives a product melting nearly 20° higher than Meyer's preparation and appears to be more economical of time and materials.

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[4] Ger. pat. 340,874 (1921); 343,054 (1922).

[5] Gilman and Pickens [This Journal, 47, 245 (1925)] present a recent summary of the theory.

[6] Meyer, *Monatsh.*, 22, 109 (1901).

Experimental Part

Nicotinyl Chloride. (a) ATTEMPTED PREPARATION BY MEYER'S METHOD.—Fifteen g. of well-dried nicotinic acid and 45.0 g. of thionyl chloride were placed in a small flask into which was wired a rubber stopper bearing a sealed capillary tube. The mixture was heated in a steam-bath for two hours. The capillary was then broken and the clear solution allowed to cool. The greater part of the substance in solution separated as white needles. After being washed with benzene and dried, these melted sharply at 148° (uncorr.). The substance absorbed moisture readily and dissolved with decomposition in cold water and in alcohol. It was moderately soluble in boiling benzene. From its properties and analysis it was the hydrochloride of nicotinyl chloride which has been imperfectly described by Laiblin[7] and by Meyer.[6]

Anal. Subs., 0.2355, 0.2497: AgCl, 0.3692, 0.3921. Calcd. for $C_6H_5ONCl_2$: Cl, 39.84. Found: 38.78, 38.85.

The reaction described above was repeated under various conditions with essentially the same results. When, however, the excess of thionyl chloride was distilled before crystallization occurred and the residue was extracted repeatedly with boiling benzene, the product then gave the properties and analysis of rather impure nicotinyl chloride. This process was not satisfactory for preparing the quantities desired, nor could pure esters be obtained from the product.

(b) THE MODIFIED METHOD.—Preliminary experiments showed that the acid chloride, mixed with only small amounts of its hydrochloride, was formed when the acid was heated with a small excess of thionyl chloride in dry benzene. After a number of trials the following procedure was adopted.

Ten g. (0.082 mole) of nicotinic acid was suspended in 75 cc. of benzene (dried over sodium) in a small flask and 14.5 g. (0.123 mole) of thionyl chloride was added. The flask was closed as described in (a) above and heated during frequent shaking in a steam-bath for two hours. The benzene was decanted while still warm and the residue of nicotinyl chloride was extracted thrice with 30cc. portions of boiling benzene to remove the hydrochloride. The product was kept over calcium chloride and paraffin wax. In four runs the yield was 88–91% of a white, semi-crystalline solid that always melted at 264–265° (uncorr.). Meyer gave 245° as the melting point of his preparation, which probably was somewhat impure.[8]

Anal. Subs., 0.2216: AgCl, 0.2166. Calcd. for C_6H_4ONCl: Cl, 25.06. Found: 24.18.

β-Diethylamino-ethyl Nicotinate (Hydrochloride).—Preliminary experiments showed that this compound could be formed by the reaction of equivalent quantities of nicotinyl chloride and β-diethylamino-ethyl alcohol in benzene solution and subsequent crystallization of the pasty product from pure acetone. The purity was somewhat higher, however, when the reaction was run in acetone solution and the product crystallized by cooling the solvent. The following procedure is typical.

Eight g. of finely powdered nicotinyl chloride was suspended in 40 cc. of acetone in a small flask. An equal volume of acetone containing 6.83 g. of the amino alcohol

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[7] Laiblin, *Ann.*, 196, 167 (1879).

[8] Compare Wolffenstein and Hartwich, *Ber.*, 48, 2043 (1915).

was gradually added during cooling and the mixture was warmed and shaken for an hour. The acetone solution was then filtered while hot from a small amount of solid and cooled to crystallization. A second crop of crystals obtained by concentrating the filtrate was united with the first and these were recrystallized from fresh solvent. From three preparations the average yield was 41% of white needles that melted gradually between 140° and 160° when slowly heated, but rather abruptly in contact with a bath previously heated to 169–170°. The substance is hygroscopic and dissolves readily in cold water and the lower alcohols, from which it cannot be crystallized.

Anal. Subs., 0.3741, 0.2655: AgCl, 0.2110, 0.1505. Calcd. for $C_{12}H_{19}O_2N_2Cl$: Cl, 13.71. Found: 13.95, 14.02.

γ-Diethylaminopropyl Nicotinate (Hydrochloride).—Four g. of nicotinyl chloride was suspended in 30 cc. of dry benzene, and 3.67 g. of γ-diethylaminopropyl alcohol in an equal volume of benzene was gradually added. Upon refluxing for an hour the nicotinyl chloride was slowly replaced by a pasty layer that collected upon the bottom of the flask. Upon triturating with fresh portions of hot benzene and cooling, the paste changed to a powdery white solid. It was brought to constant weight in a desiccator over calcium chloride and paraffin wax; yield, 90%. The substance is very hygroscopic and is readily soluble in water and the lower alcohols, but could not be crystallized from any common solvent. It melted at 172–173° in a previously heated bath.

Anal. Subs., 0.2982, 0.3158: AgCl, 0.1587, 0.1682. Calcd. for $C_{13}H_{21}O_2N_2Cl$: Cl, 13.06. Found: 13.16, 13.18.

Attempts to carry out the reaction in acetone solution appeared to give the same substance, but it could be obtained only as a semi-crystalline mass which rapidly absorbed moisture.

Pharmacological Tests

The authors are indebted to Professor P. D. Lamson of the Vanderbilt University Medical School for tests on the two compounds described above. These were applied in dilute and in concentrated solution, under a variety of conditions, to the exposed vagus nerves of anesthetized dogs, to the eyes of rabbits, and to the nerve endings of the operator's tongue. In no case was there any certain evidence of local anesthesia or of mydriatic action, and no marked irritation of the mucous membrane. The intravenous injection of as much as 150 mg. of the substances produced only a slight depression of the blood pressure and no appreciable effect on the respiration. No definite difference could be detected in the action of the two compounds, both of which are remarkably inert.

Summary

The β-diethylamino-ethyl and γ-diethylaminopropyl esters of nicotinic acid have been prepared and found to be devoid of local anesthetic properties. The preparation of nicotinyl chloride has been improved.

NASHVILLE, TENNESSEE

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UPPER SCHOOL OF AGRICULTURE OF THE REPUBLIC OF COLOMBIA]

A RAPID METHOD FOR THE DETERMINATION OF ORGANIC NITROGEN

BY G. JARAMILLO

RECEIVED JULY 3, 1926 PUBLISHED SEPTEMBER 4, 1926

The alkaline combustion of nitrogenous organic substances with evolution of ammonia can be utilized in a very simple manner for the quantitative determination of organically combined nitrogen. By heating the sample with solid sodium hydroxide and sodium acetate, all the nitrogen is evolved as ammonia in a very short time, the last traces of ammonia that would remain in the tube being expelled by the methane generated when the temperature is raised towards the end of the combustion.

We use a copper test-tube about 17.8 cm. long and 2.5 cm. in diameter, provided with a sound cork fitted with a delivery tube which leads the gases to a flask containing 25 cc. of 0.1 *N* sulfuric acid. The sample is heated in the copper tube with 1 g. of pure sodium hydroxide and 2 g. of crystallized sodium acetate. The heating is performed gently at first, while the water of crystallization of the sodium acetate is expelled, in order to avoid over-boiling of the fused mass; then the tube is strongly heated, and a copious evolution of methane begins, which is indicated by a rapid bubbling in the receiving flask with the discharge of dense white fumes. When the bubbling has ceased, the delivery tube is washed with distilled water into the flask, and the remaining acid is titrated with 0.1 *N* sodium hydroxide solution, using litmus as an indicator. This operation takes about 20 minutes. Blank determinations were made to test the purity of the reagents before the determinations were made for the analytical data given below in comparison with the results obtained by the Kjeldahl method. The operation takes about 30 minutes.

It is seen that for the substances rich in nitrogen the results obtained by

TABLE I

ANALYSES FOR NITROGEN

	Samples	Kjeldahl method, %	Alkaline combustion method, %
1	Wheat flour	2.52	2.59
2	Mixed fertilizer	2.10	2.15
3	Blood fertilizer	12.11	12.38
	Soils		
		0.15	0.15
		.07	.07
		.16	.15
		.16	.18
		.23	.23
		.17	.15

the alkaline combustion method are about 2% of the total nitrogen content higher than those obtained by the Kjeldahl method; this cannot be ascribed to sodium hydroxide particles carried off from the combustion tube, since this would make a great difference in the results for the samples of low nitrogen content; we must suppose, therefore, that there are some leakages in our distilling apparatus, or that one hour and a half of distillation is not enough to expel all of the ammonia from the solution.

For the determination of nitrogen in liquids such as milk or beer, we suggest that a measured volume of the liquid be evaporated to dryness in a shallow porcelain dish, lined inside with tin foil free from holes, in order to facilitate the transfer of the residue to the combustion tube.

Summary

A method for the determination of nitrogen by heating with solid sodium hydroxide and sodium acetate is described. The operation takes about thirty minutes.

MEDELLIN, COLOMBIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BARNARD COLLEGE]

ADDITION REACTIONS OF UNSATURATED ALPHA-KETONIC ACIDS

BY MARIE REIMER

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The action of sunlight on methyl benzalpyruvate has recently been described.[1] For further study of the effect of light on unsaturated α-ketonic esters, those of anisalpyruvic acid were chosen since it has been shown in this Laboratory[2] in a comparative study of methyl esters of benzoyl- and of anisoylacrylic acids that, whereas the former isomerizes on exposure to the light, the latter polymerizes with extreme ease. It might be expected, therefore, that the introduction of the *p*-methoxyl group into benzalpyruvic ester would increase the tendency toward polymerization already existing. Experiments have shown, however, that exposure of anisalpyruvic acid and its methyl and ethyl esters to the sunlight leads neither to polymerization nor to isomerization.

Since the polymerization of an ethylenic compound to a cyclobutane derivative is an addition reaction, whatever may be its mechanism, it seemed of interest to study the behavior of benzalpyruvic acid and of anisalpyruvic acid toward various addenda. The blocking effect of the *p*-methoxyl group in light polymerization has recently been reported also in the case of dianisalacetone by Stobbe and Färber[3] who quote, as a parallel

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[1] Reimer, THIS JOURNAL, 46, 783 (1924).

[2] Rice, *ibid.*, 45, 222 (1923); 46, 214 (1924).

[3] Stobbe and Färber, *Ber.*, 58, 1548 (1925).

case, the work of Borsche[4] who did not obtain addition products when he treated dianisalacetone with malonic and aceto-acetic esters. Kohler and his co-workers,[5] investigating these same reactions, have shown, however, that under different conditions, addition does take place although a certain amount of hindrance to the addition was noted in the case of several anisal ketones with malonic ester.

The results of experiments described in this paper are in line with those of Kohler. The reactions of benzalpyruvic and of anisalpyruvic acids with bromine, hydrogen bromide and bromine in methyl alcohol solution were studied. No essential difference in the tendency toward addition of the two ketonic acids was found. As far as one can draw conclusions from these experiments, there would seem to be no connection between ease of addition and tendency toward light polymerization.

In contrast to these results with addition reactions a number of cases have been described in which the course of a reaction has been profoundly influenced by the introduction of methoxyl groups. As examples may be given the influence of the *p*-methoxyl group on the stability of oximes[6] on the reactivity of the carbonyl group in unsaturated ketones,[7] on the ease of dissociation into free radicals[8] and on the migration of the phenyl group.[9] These properties of the *p*-methoxyl group in increasing the activity of certain types of compounds such as those just listed, on the one hand, and in blocking completely the polymerization by sunlight, on the other, are especially interesting in view of the prevalence of this group in naturally occurring compounds such as the alkaloids and the anthocyanins.

Experimental Part

Reactions with Benzalpyruvic Acid

Benzalpyruvic acid was prepared by the method previously described, with the following improvement which saves much time. The crude sodium salt from the condensation reaction should be completely dried and can then be dissolved in boiling water without danger of hydrolysis. The acid precipitated from this solution contains one molecule of water.

An interesting characteristic of the acid is the tenacity with which it holds solvent of crystallization. In one experiment in which the dry acid was crystallized from benzene, long, shining, bright yellow prisms separated; m. p., 70–76°. Analysis showed that these contained benzene. This was lost slowly on exposure to the air, the final melting point being 60–62°.

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[4] Borsche, *Ann.*, **375**, 145 (1910).

[5] Kohler and Helmkamp, This Journal, **46**, 1018 (1924). Kohler and Dewey, *ibid.*, **46**, 1267 (1924).

[6] Meisenheimer, Lange and Lamparter, *Ann.*, **444**, 94 (1925).

[7] Straus and Heyn, *Ann.*, **445**, 92 (1925).

[8] Gomberg and Buchler, This Journal, **45**, 207 (1923).

[9] McKenzie, Roger and Wills, *J. Chem. Soc.*, **129**, 780 (1926).

From aqueous solution the acid crystallizes with one molecule of water and may subsequently be crystallized several times from benzene without losing all of the crystal water. The first crystals to separate from the benzene solution are transparent, pale yellow plates; later, clumps of opaque, deeper yellow crystals appear. The clear plates melt at 55–57° and are identical with the acid crystallized from water. The opaque crystals melt at 60–62° and contain no water.

Anal. Subs. (55–57°), 0.2013: CO_2, 0.4567; H_2O, 0.0933. Calcd. for $C_{10}H_8O_3.H_2O$: C, 61.85; H, 5.15. Found: C, 61.85; H, 5.18.

Subs. (60–62°), 0.1987; CO_2, 0.4956; H_2O, 0.0897. Calcd. for $C_{10}H_8O_3$: C, 68.18, H, 4.54. Found: C, 68.03; H, 4.55.

Reaction with Bromine

Benzalpyruvic Acid Dibromide, $C_6H_5CHBrCHBrCOCOOH$.—The dibromide of benzalpyruvic acid was prepared by Erlenmeyer[10] who gives a melting point of 138° and by Ciusa,[11] who states that the substance melts at 124°. The several preparations made during this work melted anywhere from 125° to 142°. The differences are due to the ease with which the substance loses hydrogen bromide on heating, especially when moisture is present, to form the unsaturated bromo compound described below. The crude product of bromine addition is a colorless solid; m. p., 135–138°. It is readily soluble in methyl and ethyl alcohols, acetone and hot benzene, fairly soluble in ether and chloroform. From a concentrated solution of chloroform to which an equal volume of ligroin has been added it crystallizes in fine needles; m. p., 142°, with decomposition.

Anal. Subs., 0.1833: CO_2, 0.2396; H_2O, 0.0393. Calcd. for $C_{10}H_8O_3Br_2$: C, 35.71; H, 2.38. Found: C, 35.81; H, 2.41.

β-Bromobenzalpyruvic Acid, $C_6H_5CH{=}CBrCOCOOH$.—Benzalpyruvic acid dibromide was suspended in water and the mixture boiled for about ten minutes. The solid changed to a yellow oil which gradually dissolved. From the cooled solution there separated shining, colorless needles of a brilliant, pearly luster. When heated rapidly the substance melts at about 100°. When heated slowly it resolidifies in the melting-point tube and clears again at about 127°. After repeatedly heating the same sample the melting point is 131–132°. This behavior is due to the fact that the substance crystallizes with one molecule of water which it loses slowly on heating. When the low-melting form is recrystallized from benzene two kinds of crystals separate giving opaque clumps which contain water of crystallization and melt at about 100°, and fine, shining needles, m. p., 131–132°. The acid is best dehydrated by standing in a sulfuric acid desiccator for 48 hours. It is readily soluble in the usual organic solvents.

Anal. Subs. (low melting), 0.1585: CO_2, 0.2538; H_2O, 0.0492. Calcd. for $C_{10}H_7O_3Br.H_2O$: C, 43.95; H, 3.29. Found: C, 43.67; H, 3.44.

Subs. (131–132°), 0.1631: CO_2, 0.2812; H_2O, 0.0400. Calcd. for $C_{10}H_7O_3Br$: C, 47.08; H, 2.74. Found: C, 47.02; H, 2.74.

In benzene solution the acid is extraordinarily light-sensitive. These reactions will be reported in a later paper.

The position of the bromine atom in β-bromobenzalpyruvic acid was proved by identification of the product formed by its oxidation with hydrogen peroxide. The oxidation of several unsaturated α-ketonic acids with

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[10] Erlenmeyer, *Ber.*, **36**, 2527 (1903).

[11] Ciusa, *Gazz. chim. ital.*, [i] **49**, 164 (1919).

hydrogen peroxide has been described.[12] The authors used alcoholic solutions and make the statement that good yields of product were obtained only when no excess of reagent was used, except in one case, that of anisalpyruvic acid, where 1.5 molecular proportions was needed. In the present work aqueous solutions of the sodium salts of the acids were used and a large excess of hydrogen peroxide did not decrease the yield of product which was quantitative in all the reactions. From β-bromobenzalpyruvic acid an acid was obtained which separated from boiling water in long, shining needles; m. p., 130–131°. It was proved to be *trans*-α-bromocinnamic acid by a mixed-melting-point determination with that substance prepared by elimination of hydrogen bromide from cinnamic acid dibromide and subsequent isomerization of the *allo*-α-bromocinnamic acid (m. p., 120°) which was the chief product of this reaction.[13]

Methyl β-Bromobenzalpyruvate, $C_6H_5CH{=}CBrCOCOOCH_3$.—This ester is not formed by treating the acid with methyl alcohol saturated with hydrogen chloride; the acid crystallized from the solution unchanged. The ester was prepared by elimination of hydrogen bromide from the dibromide of methyl benzalpyruvate.

The *methyl ester of benzalpyruvic acid dibromide*, prepared by addition of bromine to methyl benzalpyruvate, is a stable substance that crystallizes from methyl alcohol in pale, straw-colored needles; m. p., 117°.

Anal. Subs., 0.1929: CO_2, 0.2665; H_2O, 0.0503. Calcd. for $C_{11}H_{10}O_3Br_2$: C, 37.71; H, 2.85. Found: C, 37.77; H, 2.89.

Four g. of this ester in 75 cc. of methyl alcohol was boiled for one hour with 2.2 g. of potassium acetate. The filtered solution was allowed to evaporate spontaneously. The clear, yellow oil remaining was dissolved in ether, the solution washed, dried and the solvent evaporated. The oil remaining was analyzed.

Anal. Subs., 0.1845: CO_2, 0.3308; H_2O, 0.0635. Calcd. for $C_{11}H_9O_3Br$: C, 49.07; H, 3.34. Found: C, 48.89; H, 3.78.

As alkaline solution attacked the double linkage, the ester was hydrolyzed by boiling with concd. hydrochloric acid. β-Bromobenzalpyruvic acid crystallized from the solution.

Experiments with Hydrogen Bromide

No addition product with hydrogen bromide could be isolated. The ease with which the dibromo addition product loses hydrogen bromide readily accounts for this fact.

Reaction with Bromine in Methyl Alcohol Solution

A methyl hypobromite addition product is not formed by the method described by Conant and Jackson.[14] The experiment was carried out at 0°, at room temperature and with ethyl as well as methyl alcohol, with the same results.

Fifteen g. of benzalpyruvic acid was dissolved in 375 cc. of 85% methyl alcohol. A stream of dry air carrying bromine vapor was bubbled through the solution for eight

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[12] Lubryzsiska and Smedley, *Biochem. J.*, **7**, 375 (1913).

[13] Sudburough and Thompson, *J. Chem. Soc.*, **83**, 673 (1903).

[14] Conant and Jackson, This Journal, **46**, 1727 (1924).

to ten hours until 5.9 g. of bromine had been decolorized. The alcohol was then distilled and the residue, consisting of oil and a small amount of water, cooled. The aqueous layer was soon filled with white crystals. These were filtered off and the oil remaining was extracted repeatedly with 100cc. portions of ice water which quickly filled with the same white solid. This was proved to be β-bromobenzalpyruvic acid (m. p., about 100°) with water of crystallization previously described. The oily residue from which no more solid could be extracted with water, was dissolved in ether and the solution dried. Evaporation of the solvent left an oil which gradually deposited anhydrous *β-bromobenzalpyruvic acid; m. p., 130–131°. The oil remaining gave analytical results* agreeing with those for a methyl hypobromite addition product. On exposure in a thin layer to the air, however, it deposited very slowly crystals of β-bromobenzalpyruvic acid (m. p., 130–131°) and evidently was this acid in combination with a molecule of methyl alcohol.

Anal. Subs., 0.1722: CO_2, 0.2923; H, 0.0606. Calcd. for $C_{10}H_7O_3Br.CH_3OH$: C, 45.99; H, 3.83. Found: C, 46.29; H, 3.91.

The only reaction with bromine in methyl alcohol solution was addition of bromine and subsequent loss of hydrogen bromide. A 95% yield of product was obtained.

Reactions with Anisalpyruvic Acid[15]

It is noteworthy that anisalpyruvic acid is much more stable toward alkaline reagents than the corresponding unsubstituted acid, so that the strongly alkaline reaction mixture may stand for many hours without reversal of the reaction. It was prepared by a modification of the method of Ciusa.[11]

Forty g. of pyruvic acid, 68.5 g. of anisic aldehyde and 300 cc. of 10% aqueous sodium hydroxide were brought together at 0° and the mixture was vigorously stirred. After ten minutes a gelatinous paste separated. The yield of product was very small unless this mixture was allowed to stand for at least 12 hours. After this length of time a hard, crystalline mass of sodium anisalpyruvate had formed. This was filtered off, air-dried, dissolved in boiling water and the solution acidified. The bright yellow acid, crystallized from water, melts at 131°. (Ciusa's melting point of 81° is evidently that of the acid with alcohol of crystallization.) The acid is the *trans* form since, on oxidation with hydrogen peroxide, a quantitative yield of *trans-p*-methoxycinnamic acid was obtained, which showed the characteristic behavior of "liquid crystals," melting to an opaque liquid at 170° and to a clear liquid at 185°.[16] It was identified by a mixed-melting-point determination with the acid prepared by Perkin's synthesis.

The *methyl ester* was prepared by dissolving 14 g. of acid in 50 cc. of methyl alcohol saturated with hydrogen chloride. Almost immediately the pale yellow, shining crystals of the methyl ester separated. The ester, crystallized from methyl alcohol, melts at 106°. It is readily soluble in chloroform and acetone, fairly soluble in ether, benzene and alcohol, very slightly soluble in ligroin.

Anal. Subs., 0.1649: CO_2, 0.3964; H_2O, 0.0827. Calcd. for $C_{12}H_{12}O_4$: C, 65.45; H, 5.45. Found: C, 65.55; H, 5.57.

The *ethyl ester* was prepared in the same way. It separated from concentrated alcoholic solution in brilliant, pale yellow plates; m. p., 48°. It is much more soluble in the usual organic solvents than the methyl ester.

Anal. Subs., 0.1633: CO_2, 0.3988; H_2O, 0.0915. Calcd. for $C_{13}H_{14}O_4$: C, 66.66, H, 5.98. Found: C, 66.60; H, 6.22.

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[15] With Alice L. Kreissl.

[16] Rotarski, *Ber.*, 41, 1994 (1908).

Reactions with Bromine

Anisalpyruvic Acid Dibromide, 4-$CH_3O.C_6H_4CHBrCHBrCOCOOH$.—The dibromo addition compound was prepared in quantitative yield by addition of bromine to the cooled chloroform solution of anisalpyruvic acid. The substance is slightly less stable than benzalpyruvic acid dibromide and could not be purified by recrystallization. The crystals that separated from chloroform and ligroin or from glacial acetic acid were a mixture of the dibromo and the unsaturated monobromo acids. The crude product, m. p. 98–100°, was used for analysis.[17]

Anal. Subs., 0.1779: CO_2, 0.2362; H_2O, 0.0403. Calcd. for $C_{11}H_{10}O_4$: C, 36.06; H, 2.72. Found: C, 36.20; H, 2.52.

The *methyl ester* was prepared by addition of bromine to a cooled chloroform solution of methylanisalpyruvate. The solid melting at 93° was washed with methyl alcohol and analyzed.

Anal. Subs., 0.1757: CO_2, 0.2212; H_2O, 0.0471. Calcd. for $C_{12}H_{12}O_4Br_2$: C, 37.89; H, 3.15. Found: C, 37.76; H, 2.97.

The *ethyl ester* prepared in the same way was left as a colorless oil on evaporation of the chloroform. It solidifies when treated with cold ethyl alcohol but must be handled quickly as it decomposes on exposure to the air. The solid, m. p. 100–108°, washed with alcohol, was used for analysis.

Anal. Subs., 0.1567: CO_2, 0.2290; H_2O, 0.0560. Calcd. for $C_{13}H_{14}O_4Br_2$: C, 39.59; H, 3.52. Found: C, 39.82; H, 3.33.

β-Bromo-anisalpyruvic Acid, 4-$CH_3OC_6H_5CH{=}CBrCOCOOH$.—The substance was prepared by boiling the dibromo acid in water, from which it separates in shining, cream-colored plates. The purest specimen was obtained by dissolving the acid in hot glacial acetic acid and adding an equal volume of hot water. The lustrous crystals that separated contained one molecule of water and melted at 100° to 125°. Different specimens of this acid have various amounts of water so that they may begin to melt as low as 85°. The acid dried over sulfuric acid melted at 136°.

Anal. Subs. (low melting), 0.1402: CO_2, 0.2236; H_2O, 0.0465. Calcd. for $C_{11}H_9O_3Br.H_2O$: C, 43.56; H, 3.63. Found: C, 43.49; H, 3.69.

Subs. (136°), 0.1497: CO_2, 0.2559; H_2O, 0.0466. Calcd. for $C_{11}H_9O_3Br$: C, 46.31; H, 3.15. Found: C, 46.61; H, 3.45.

The substance is readily soluble in the usual organic solvents except ligroin in which it is very slightly soluble.

There is no esterification when this acid is allowed to stand for many hours in methyl alcohol saturated with hydrogen chloride. This behavior is like that of β-bromobenzalpyruvic acid. To prove the structure of this acid it was oxidized with hydrogen peroxide.

α-Bromo-*p*-methoxycinnamic Acid, 4-$CH_3OC_6H_4CH{=}CBrCOOH$.—The product of oxidation of β-bromo-anisalpyruvic acid with hydrogen peroxide crystallized from boiling water in pale, straw-colored needles. A purer product is obtained from methyl alcohol from which it separates in stiff, almost colorless needles; m. p., 188°. The acid is soluble in methyl and ethyl alcohols, ether and acetone, fairly soluble in glacial acetic acid and chloroform.

Anal. Subs., 0.1159: CO_2, 0.1967; H_2O, 0.0374. Calcd. for $C_{10}H_9O_3Br$: C, 46.68; H, 3.50. Found: C, 46.28; H, 3.57.

The position of the bromine atom is indicated by the fact that the acid decolorizes potassium permanganate solution in the cold with the odor of anisic aldehyde.

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[17] Ciusa's melting point of 125° must be that of the unsaturated bromo acid.

The *methyl ester* was prepared in quantitative yield by allowing a saturated solution of hydrogen chloride in methyl alcohol to stand in contact with the acid overnight. It crystallizes from a small volume of methyl alcohol in stiff, colorless needles; m. p., 55°.

Anal. Subs., 0.1722: CO_2, 0.3065; H_2O, 0.0635. Calcd. for $C_{11}H_{11}O_3Br$: C, 48.70; H, 4.05. Found: C, 48.54; H, 4.09.

On hydrolysis a quantitative yield of the acid (188°) was obtained. For identification of this acid, attempts were made to prepare it from *p*-methoxycinnamic acid dibromide. In this reaction an unstable, isomeric acid (155°) was obtained. From the ester of the dibromide, however, the stable acid (188°) was prepared. The treatment of *p*-methoxycinnamic acid dibromide with aqueous potassium hydroxide is described by Eigel,[18] who obtained *p*-methoxyphenyl-bromo-ethylene, $CH_3OC_6H_4CH = CHBr$ (m. p., 55°), as the only product. By using potassium acetate, however, an acid product also is obtained. Five g. of *p*-methoxycinnamic acid dibromide was suspended in 50 cc. of alcohol, 2.7 g. of potassium acetate added and the mixture was boiled for several hours. The alcohol was then evaporated and the aqueous solution of the residue extracted with ether. The ether, after repeated washing with sodium carbonate solution, deposited a quantity of the substituted ethylene melting at 55°. The sodium carbonate washings on acidification gave a small amount of acid melting at about 155° after repeated crystallization from methyl alcohol.

Anal. Subs., 0.1573: CO_2, 0.2678; H_2O, 0.0613. Calcd. for $C_{10}H_9O_3Br$: C, 46.68; H, 3.50. Found: C, 46.43; H, 4.32.

Esterification of this acid gave an oil from which no crystalline compound could be obtained. Hydrolysis of this oil with a strong solution of potassium hydroxide in methyl alcohol gave a crystalline potassium salt which separated almost immediately. This was filtered off, dissolved in water and the solution acidified. The colorless precipitate was pure acid; m. p., 188°. The acid melting at 155° had, therefore, isomerized during some stage of the reaction to the higher-melting acid and is, then, the unstable geometrical isomer of this acid. This high-melting acid (188°) can be obtained in good yield by treating the methyl ester of *p*-methoxycinnamic acid dibromide with 10% alcoholic potassium hydroxide in the cold. The potassium salt, which separated rapidly in 75% yield, deposited pure acid, m. p. 188°, on acidification of its solution. This experiment was carried out by Eigel,[18] who did not investigate the mixture of impure acids that he obtained.

With hydrogen bromide, anisalpyruvic acid does not react.

Reaction with Bromine in Methyl Alcoholic Solution

When anisalpyruvic acid was treated with bromine in aqueous methyl alcoholic solution, different substances were obtained, depending on the speed with which the bromine was carried into the solution. From none of the experiments was any methyl hypobromite addition compound obtained; in all of them there was a considerable quantity of oil that could not be purified, together with various amounts of crystalline product.

The reaction was carried out as previously described in the case of benzalpyruvic acid. The brownish oil left after removal of the alcohol from the reaction product gradually deposited crystals. These were filtered out and further amounts of crystalline compound obtained by treating the remaining oil with benzene. When the bromine vapor was carried through the solution very slowly (10–12 hours), the crystals were found to be hydrated β-bromo-anisalpyruvic acid; m. p., 90–100°. From 15 g. of anisalpyruvic acid, 12 g. of unsaturated bromo acid was obtained.

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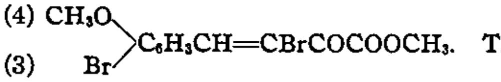
[18] Eigel, *Ber.*, 20, 2537 (1887).

A more rapid reaction (four to five hours) gave a compound that crystallized from the oily reaction product in stiff, compact needles. Three g. was obtained from 15 g. of the original acid. The only other crystalline product of this reaction was the hydrated β-bromo-anisalpyruvic acid (90–100°). The new crystalline compound was crystallized from a large volume of boiling methyl alcohol from which it separated in fine, pale yellow needles; m. p., 145°.

Anal. Subs., 0.1455: CO_2, 0.2047; H_2O, 0.0365. Calcd. for $C_{12}H_{10}O_4Br_2$: C, 38.09; H, 2.64. Found: C, 38.36; H, 2.78.

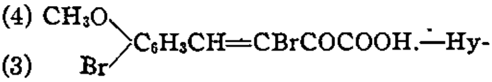
The compound is an ester and is unsaturated since its acetone solution instantly decolorizes potassium permanganate in the cold. The product of this oxidation, an acid containing bromine, m. p. 212°, was proved to be 3-bromo-anisic acid by a mixed-melting-point determination with that acid prepared by bromination of anisic acid. The ester (145°) is, therefore, methyl β-bromo-3-bromo-anisalpyruvate,



$$\begin{matrix}(4)\ CH_3O\\ (3)\ \ Br\end{matrix}\!>\!C_6H_3CH{=}CBrCOCOOCH_3.$$

The rapid reaction with bromine and methyl alcohol has caused bromine to enter the ring as well as to add at the double linkage and has brought about esterification of the acid.

β-Bromo-3-bromo-anisalpyruvic Acid,



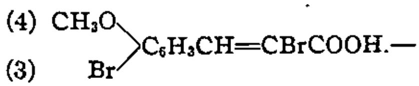
$$\begin{matrix}(4)\ CH_3O\\ (3)\ \ Br\end{matrix}\!>\!C_6H_3CH{=}CBrCOCOOH.$$

—Hydrolysis of the ester (m. p., 145°) was carried out by treating it with just enough of a 0.5% solution of potassium in methyl alcohol to bring it into solution. After an hour the potassium salt that had separated was filtered out, dissolved in water and the solution acidified. The yellowish acid that separated holds water of crystallization which accounts for its low, irregular melting point of about 135°. It was crystallized once from boiling water and analyzed.

Anal. Subs., 0.1497: CO_2, 0.1959; H_2O, 0.0330. Calcd. for $C_{11}H_8O_4.{}^1/_2H_2O$: C, 35.38; H, 2.41. Found: C, 35.68; H, 2.44.

From a solution of this acid in methyl alcohol saturated with hydrogen chloride the characteristic pale yellow needles of the ester (m. p., 145°) separated in quantitative yield.

α-Bromo-3-bromo-4-methoxycinnamic Acid,



$$\begin{matrix}(4)\ CH_3O\\ (3)\ \ Br\end{matrix}\!>\!C_6H_3CH{=}CBrCOOH.$$

—By oxidation of the acid just described with hydrogen peroxide a colorless acid, m. p. 181°, was obtained. It was proved to be α-bromo-3-bromo-4-methoxycinnamic acid by preparing it from 3-bromo-4-methoxycinnamic acid dibromide. This substance, melting at 162°, was studied by Eigel[18] who did not obtain an acid product when he treated it with potassium hydroxide. The acid (m. p., 181°) can be obtained from it, however, by hydrolysis of the ester formed by dissolving 3-bromo-4-methoxycinnamic acid dibromide in methyl alcohol and hydrochloric acid. This mixture was allowed to stand overnight, then poured into dil. sodium carbonate solution and the solution extracted with ether. On evaporation of the ether an ester separated in hard, shining clumps. After crystallization from a small volume of boiling methyl alcohol it melted at 91°.

Anal. Subs., 0.1523: CO_2, 0.2089; H_2O, 0.0496. Calcd. for $C_{11}H_{10}O_3Br_2$: C, 37.71; H, 2.85. Calcd. for $C_{11}H_{11}O_3Br_3$: C, 30.62; H, 2.65. Found: C, 37.40; H, 3.60.

The tribromide has evidently lost hydrogen bromide on esterification. The ester is that of α-bromo-3-bromo-4-methoxycinnamic acid. By hydrolysis with a concentrated alcoholic solution of potassium hydroxide a potassium salt separated which, on acidification of its solution, gave the acid melting at 181°.

In his discussion of bromomethoxycinnamic acid dibromide (m. p., 162°) Eigel states that it is decomposed by water and alcohol but gives no account of the decomposition products. In an attempt to prepare the acid (m. p., 181°) in quantity, this decomposition was investigated. Four g. of the acid (m. p., 162°) was suspended in 120 cc. of cold water and the mixture allowed to stand for 12 hours and frequently shaken. The flocculent, pure white solid which separated was filtered off, washed with water and crystallized from a small volume of methyl alcohol; yield, 80%. The solid has the properties of the substance obtained by Eigel by hydrolysis of the acid (m. p., 162°), described by him and quoted in the new edition of Beilstein as "2- or 3-bromo-4-methoxyphenylacetylene." It crystallizes in leaves, melts at 76°, is volatile with water vapor and gives a greenish precipitate when its alcoholic solution is treated with an aqueous solution of ammoniacal cuprous chloride. The appearance and the odor of the substance are, however, exactly like those of bromo-*p*-methoxyphenylethylene (m. p., 55°) previously described. Analysis proves that it is in reality an ethylenic compound.

Anal. Subs., 0.1570: CO_2, 0.2149; H_2O, 0.0455. Calcd. for $C_9H_8OBr_2$: C, 36.98; H, 2.74. Calcd. for C_9H_7OBr: C, 51.18; H, 3.31. Found: C, 37.33; H, 3.22.

The compound was recovered unchanged from boiling alcoholic and from boiling aqueous potassium hydroxide solutions. The same compound was obtained by boiling bromomethoxycinnamic acid dibromide (m. p., 162°) with 30% aqueous potassium hydroxide for one-half hour. The greenish, crystalline precipitate formed by treatment of its alcoholic solution with aqueous ammoniacal cuprous chloride solution was proved to be the original substance precipitated from alcoholic solution by the addition of water.

Oxidation of the ethylenic compound (m. p., 76°) with a solution of potassium permanganate gave 3-bromo-anisic acid, thus establishing the position of the bromine atom in the ring.

Summary

The reactions of benzalpyruvic acid and of anisalpyruvic acid with bromine, hydrogen bromide and bromine in methyl alcoholic solution have been studied. No essential difference in the tendency toward addition of the two ketonic acids was found. They both gave quantitative yields of dibromo addition products; the bromine atom β to the ketone group was readily eliminated as hydrogen bromide to form β,γ unsaturated β-bromo-α-ketonic acids. As was to be expected from this behavior, no addition product with hydrogen bromide was formed. Addition of bromine in methyl alcoholic solution yielded not a methyl hypobromite addition product, but compounds formed by addition of bromine and subsequent loss of hydrogen bromide.

For identification of the products formed, the oxidation of the products by hydrogen peroxide was studied and a number of substituted cinnamic acids were prepared.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF IOWA STATE COLLEGE]

ORGANOCALCIUM IODIDES

BY HENRY GILMAN AND FERDINAND SCHULZE

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Introduction

In connection with studies on the mechanism of some reactions involving organomagnesium halides it is necessary to replace the —MgX group of the intermediate compound by another in order to get a compound that lends itself to ready identification. Unfortunately this is not always possible. Accordingly, a study has been made of the related organocalcium iodides in order to determine whether the —CaI group is more suitable for such replacements than is the —MgX group.

Beckmann[1] has made the only extensive study of organocalcium halides. Dufford, Nightingale and Calvert[2] investigated the luminescence of phenylcalcium and ethylcalcium iodides, and Gilman and Pickens[3] used phenylcalcium iodide in a study of the mechanism of the reduction of azobenzene by organometallic halides.

A number of experiments have shown that the organocalcium halides are generally devoid of any promise in the reactions that have made the organomagnesium halides so useful. First, the formation of organocalcium halides appears to be restricted to iodides. Second, only primary alkyl iodides undergo reaction with calcium. Even in this limited category there is an exception, for benzyl iodide gave no positive test to indicate the formation of benzylcalcium iodide. Third, the reaction between the alkyl iodide and calcium is quite sluggish and irregular and not always certain. Fourth, the yields of organocalcium iodides are far from satisfactory. This is due in part to a pronounced coupling side reaction leading to the formation of R–R compounds. Fifth, the organocalcium iodides are less reactive generally than the corresponding organomagnesium halides.

Contrary to the results of Beckmann,[1] the organocalcium iodides are not sparingly soluble in ether. The solid compound invariably deposited during the preparation of organocalcium iodide is not the organometallic halide. Instead it is very probably the di-etherate of calcium iodide.

Experimental Part

Preparation of Organocalcium Iodides.—The start and progress of the reaction between calcium and iodide vary with the kind of calcium and the degree of fineness. A variety of rasped calcium obtained from Kahlbaum was somewhat less active than shavings freshly turned from sticks of calcium. Even a given type of calcium gave irregular results, depending

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[1] Beckmann, *Ber.*, **38**, 904 (1905).

[2] Dufford, Nightingale and Calvert, THIS JOURNAL, **47**, 95 (1925).

[3] Gilman and Pickens, *ibid.*, **47**, 2406 (1925).

in large part on exposure to the atmosphere. The material was always covered, prior to use, with kerosene. However, even such covered calcium tarnished when the containers were loosely stoppered. The tarnished material entered very sluggishly into reaction with the iodides and therefore was not used.

It is necessary to use a higher concentration of iodine in ether to catalyze reactions with calcium than is needed with magnesium. The beginning of reaction between calcium and the organic iodide is shown by the disappearance of the free iodine used to catalyze the reaction, followed by the formation of a light gray or white precipitate. At times the reaction is brisk enough to cause the ether to reflux gently. These changes cannot be taken as absolute criteria for the formation of organocalcium iodides, inasmuch as the organocalcium iodides appear to have a pronounced tendency to couple with the excess of alkyl or aryl iodide that is generally present. The color test with Michler's ketone, previously described by Gilman and Schulze,[4] is reliable.

The reaction between calcium and the alkyl or aryl iodide in ether can be carried out in the conventional three-necked flask provided with a mechanical stirrer, or the reactants can be sealed in a glass container that is shaken mechanically at room temperature. The latter arrangement offers certain advantages in some preparations. Reaction between ethyl iodide in ether and calcium started in various experiments over a time range of 15 minutes to six hours. *n*-Butyl iodide started to react after ten hours, and in one experiment after 48 hours. However, the same halide when shaken in a sealed tube gave a positive test[4] after two hours. *n*-Octyl iodide gave a positive test after being shaken for 24 hours in a sealed glass container. Iodobenzene, when stirred with ether, a little iodine and calcium in a three-necked flask, gave a positive test in some cases after two hours and in others up to seven and one-half hours. In one experiment, when stirring was not used, a positive test was obtained only after 72 hours.

Ethyl bromide, *iso*propyl iodide, *tert.*-butyl iodide, benzyl bromide and benzyl iodide gave no positive tests after being shaken with calcium. The *tert.*-butyl iodide underwent a reaction but there was no positive test for the corresponding organocalcium iodide.[5] Benzyl iodide when shaken

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[4] Gilman and Schulze, THIS JOURNAL, 47, 2002 (1925). Unpublished work on calcium, barium and strontium dialkyls and diaryls shows that all of these organometallic compounds give positive tests. The color test with beryllium diaryls is not conclusive.

[5] *tert.*-Butyl bromide in ether reacts with *magnesium*. However, a positive test is obtained only when the Michler's ketone solution[4] is added in the early part of the vigorous reaction. When the ether has ceased to boil no positive test is obtained. Preliminary experiments indicate that the *tert.*-butylmagnesium iodide that is first formed undergoes dissociation to magnesious bromide (—MgBr) and the *tert.*-butyl radical [$(CH_3)_3C$-]. The radical then appears to undergo a considerable disproportionation to trimethylmethane [$(CH_3)_3CH$] and *iso*butylene [$(CH_3)_2C = CH_2$]. Gomberg has given an excellent proof for existence of the magnesious halides [*Chem. Rev.*, 2, 301

in a sealed bottle for two to three weeks also underwent a reaction but gave no positive test.

It was hoped that the secondary reaction between organocalcium iodides and alkyl iodides could be overcome by removing the organocalcium halide as fast as it formed. For this purpose, advantage was taken of the very suggestive experiments made by Gilliland and Blanchard.[6] They prepared phenylmagnesium bromide by allowing an ethereal solution of bromobenzene to descend through a column of magnesium turnings, the solution being highly diluted, before reaching the column, by the ether condensed from the vapors of the solution boiling in the receiving flask. In this manner there is a minimal contact between the organometallic halide and the organic halide from which it is prepared. However, the same principle when extended to the preparation of ethylcalcium iodide was found to be unsuccessful. When an ethereal solution of ethyl iodide was percolated through a column of calcium shavings contained in a tube 20 cm. long and 1.5 cm. in diameter, the reaction could be started only by using a concentrated solution of iodide in ether. The reaction, once started, was quite irregular. When the concentration of ethyl iodide was low, the reaction stopped altogether; when the solution was sufficiently concentrated to insure a continuous reaction, very little ethylcalcium iodide formed, probably as a result of the coupling reaction mentioned above. It is, of course, possible that the ethylcalcium iodide owes its gradual disappearance to a partial dissociation of the kind described in Ref. 5. A further difficulty in the use of the column of calcium is the marked clogging due to the deposition of the di-etherate of calcium iodide. Quite probably there is an effective concentration of ethyl iodide to warrant the use of the column, but such optimal conditions were not further investigated.

Ethylcalcium Iodide.—The white precipitate that forms when calcium reacts with ethyl iodide in ether was analyzed by Beckmann,[1] and he concluded that it was the mono-etherate of ethyl-calcium iodide, $C_2H_5CaI.(C_2H_5)_2O$. This formula is very probably incorrect, for apparently the same compound is formed when calcium undergoes reaction with any alkyl iodide. In no case did it give a positive color test[4] for an organocalcium iodide after being filtered and washed with anhydrous ether. When organocalcium iodides were shown to be present by the preparation of characteristic derivatives, the perfectly clear supernatant liquid always gave a positive color test, whereas the precipitate never gave a test. Evidently the few organocalcium iodides that were studied are soluble in ether. However, since they never were obtained in high yields no reasonable predictions can be made concerning their solubility in more concentrated solutions.

(1925)] and a study in this Laboratory of the mechanism of the reduction of azobenzene by organomagnesium halides and magnesious iodide supports his results

References to other mechanisms for the diminution in yield of organomagnesium halides are given in Ref. 2 of a paper by Gilman and Kirby [This Journal, 48, 1733 (1926)].

[6] *Gilliland and Blanchard, ibid.*, 48, 410 (1926).

It is difficult to obtain a perfectly pure sample of the white precipitate.[7] The compound is usually contaminated with bits of unaltered calcium, calcium oxide, basic calcium iodide and possibly calcium hydroxide. Because of these impurities not much reliance can be placed on the calcium analysis made by Beckmann,[1] and the only quantitative analysis he made was for calcium. A fairly homogeneous sample was obtained by treating calcium with a liberal excess of ethyl iodide in a dry atmosphere. The material was rapidly filtered, washed with anhydrous ether, transferred to a glass-stoppered weighing bottle and dried in a vacuum desiccator.

A sample prepared in this manner for analysis contained 58.18 and 57.97% of iodine. The compound that best agrees with such results is the di-etherate of calcium iodide, $CaI_2.2(C_2H_5)_2O$, which contains 57.4% of iodine. Beckmann's ethylcalcium iodide mono-etherate, $C_2H_5CaI.(C_2H_5)_2O$, contains 46.9% of iodine. A gas is evolved when this solid is treated with water. Beckmann stated that the gas was ethane contaminated with some ether. The gas was not unsaturated, and its characteristic ethereal odor coupled with its complete solubility in concd. sulfuric acid indicated that it was ether and not ethane. Two samples were analyzed.

Anal. Subs., 0 3382, 0.2944: 37.3, 32.7 cc. of gas (corr.). Calcd. for $CaI_2.2(C_2H_5)_2O$: 34.2, 29.8 cc.

The small amount of ethylcalcium iodide present accounts in part for the lack of success in obtaining characteristic anilides with phenyl- and naphthylisocyanates. However, another alkylcalcium iodide (*n*-butyl) gave the characteristic anilide with α-naphthylisocyanate.

***n*-Butylcalcium Iodide.**—When 12 g. (0.3 mole) of calcium was treated with 55.2 g. (0.3 mole) of *n*-butyl iodide in 100 cc. of ether, considerable insoluble material was deposited During the preparation, about 2 liters of gas was evolved. The gas was saturated, inflammable and insoluble in concd. sulfuric acid. Undoubtedly it was largely *n*-butane, formed by the reaction of a trace of moisture in the reagents with *n*-butylcalcium iodide.

After the reaction had been allowed to complete itself, over two days, the mixture was hydrolyzed with dil. hydrochloric acid. Considerable heat is evolved during the hydrolysis of any organocalcium halide, and a part of this is very probably due to the hydration of calcium iodide. The ethereal layer was separated, dried and 10 g. of liquid was obtained; b. p , 120–130°. If the mixture were entirely *n*-octane this would correspond to a 59% yield. However, *n*-butyl alcohol and *n*-butyl iodide might have been contained in this fraction. Accordingly, the mixture was first refluxed for four hours with 10% sodium hydroxide solution; this was then extracted with ether, the etheral solution carefully shaken with concd. sulfuric acid to remove ether and *n*-butyl alcohol, and finally fractionally distilled. In this way, despite mechanical losses, there was obtained a 29.2% yield of *n*-octane.

In another run the *n*-butylcalcium iodide was characterized by the preparation of *n*-valeryl-α-naphthalide obtained from the reaction with α-naphthylisocyanate.

***n*-Octylcalcium Iodide.**—A mixture of 0.05 mole of calcium and an equivalent amount of *n*-octyl iodide in an excess of ether was shaken for 24 hours in a sealed flask. A heavy, white precipitate formed and the supernatant liquid gave a positive color test for *n*-octylcalcium iodide. After hydrolysis, the ether layer yielded 2 g. or a 17.8% yield of hexadecane, $C_{16}H_{34}$.

Phenylcalcium Iodide.—Phenylcalcium iodide was treated with phenylisocyanate,

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[7] Experiments now in progress show that it is possible to prepare unusually pure, ether-free organomagnesium halides in a special apparatus through which circulates pure, dry hydrogen.

and to the reaction mixture was then added a slight excess of diethyl sulfate. After refluxing for an hour, the mixture was hydrolyzed and then worked up in the customary manner. Some benzanilide, the normal reaction product of phenylcalcium iodide and phenylisocyanate, was obtained. Practically all of the diethyl sulfate was recovered, and there was no indication of the formation of the desired imino ether, $C_6H_5N=C(OC_2H_5)(C_6H_5)$. This ether would have resulted by the replacement of the —CaI group attached to oxygen by an ethyl group of diethyl sulfate.[8]

A vigorous reaction occurs during the addition of an equivalent of benzoyl chloride to phenylcalcium iodide. At the end of the addition there was a strong test for phenylcalcium iodide, and benzoyl chloride was present as evidenced by its characteristic odor. In order to complete the reaction, the mixture was refluxed for 24 hours. Even after this protracted digestion of a 0.1-mole run, there was present in the mixture not only benzoyl chloride, as might have been expected, but also some phenylcalcium iodide. This emphasized in a striking manner the relatively less activity of organocalcium iodides when compared with the corresponding organomagnesium halides.[9] On working up the hydrolyzed reaction products, there were obtained a 35% yield of iodobenzene and 5% of triphenylmethane. The triphenylmethane probably owes its formation to the reduction of triphenylcarbinol when the unaltered calcium reacts with water during hydrolysis.

In another experiment the reaction between phenylcalcium iodide and benzoyl chloride was forced by refluxing for several hours in an ether-benzene solution. Under these conditions the phenylcalcium iodide was used up, and about 1% of triphenylcarbinol was obtained in addition to some unaltered iodobenzene and benzoyl chloride, benzoic acid and a small amount of an apparently intractable tar.

Despite the significant amounts of iodobenzene recovered, it appears that phenylcalcium iodide is obtained in higher yields than the other organocalcium iodides that were studied. With this arylcalcium iodide less of the di-etherate of calcium iodide separates than is the case with the alkyl calcium iodides.

Summary

Organocalcium iodides can be prepared in poor yields from a limited class of iodides. They are soluble in ether and less reactive than the corresponding organomagnesium halides.

AMES, IOWA

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[8] Under like conditions, phenylmagnesium bromide also gives benzanilide and there is no replacement of the —MgX group by an ethyl group. Compare Gilman and Kinney, THIS JOURNAL, 46, 493 (1924).

[9] In this connection mention should be made of the unreactivity of phenylcalcium iodide towards azobenzene [Gilman and Pickens, *ibid.*, 47, 2406 (1925)]. Also, unpublished results show that acid chlorides undergo ready reaction with organo-magnesium halides to give good yields of tertiary alcohols.

[Contribution from the Chemical Laboratory of Harvard University]

THE IRREVERSIBLE REDUCTION OF ORGANIC COMPOUNDS
III. THE REDUCTION OF AZO DYES

By James B. Conant and Malcolm F. Pratt

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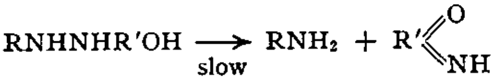
It has been shown[1] that in many instances the irreversible reduction of an organic compound may be formulated in electrochemical terms by determining the "apparent reduction potential" (A. R. P.). This has been defined as the normal potential of the reversible system that will just cause appreciable reduction (20–30% in 30 minutes) under the conditions specified. This method of investigating and formulating irreversible reduction processes can be employed only if the speed of the reduction is a function of the potential of the reagent employed. This point can be tested by examining the behavior of the compound in question with a series of graded reducing agents of known potential.

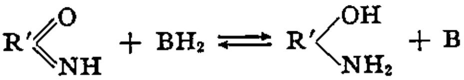
If the action of these reagents is a function of their potential the determination of an "apparent reduction potential" will be possible. The reduction of unsaturated 1,4 diketones and certain related substances, of many nitro compounds and azo dyes has been investigated in this way. In this paper we shall present some further experiments with certain hydroxy-azo dyes. These experiments confirm and amplify our general theory of irreversible reduction and in addition afford some quantitative information in regard to the relationship between structure and ease of reduction.

A relationship between the speed of reduction and the potential of the reagent is to be expected only if some reversible step controls the rate of the process.[2] The complete reduction of azo dyes according to the equation, $RN = NR'OH + 2BH_2$ (reducing agent) $\longrightarrow RNH_2 + R'(OH)NH_2 + 2B$ is irreversible, but as our preliminary work showed, the process can be formulated in terms of the potential of the reagent employed. The most probable mechanism to account for this is given below, in which Step *a* is reversible and rapid and Step *b* is irreversible and slow in comparison with Steps *a* and *c*. The reduction of the quinon-imine (Step *c*) would be expected to be very rapid and practically complete with the reducing agents necessary for the reduction of azo dyes; the question of

$$RN = NR'OH + BH_2 \rightleftharpoons RNHNHR'OH + B \qquad (a)$$



$$RNHNHR'OH \xrightarrow[\text{slow}]{} RNH_2 + R'\left\langle\begin{matrix}O\\NH\end{matrix}\right. \qquad (b)$$



$$R'\left\langle\begin{matrix}O\\NH\end{matrix}\right. + BH_2 \rightleftharpoons R'\left\langle\begin{matrix}OH\\NH_2\end{matrix}\right. + B \qquad (c)$$

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[1] Conant and Lutz, This Journal, 45, 1047 (1923); 46, 1254 (1924).

[2] Conant, *Chem. Rev.*, 3, 1 (1926).

its reversibility is not involved in this discussion. It is evident that if this mechanism is correct the rate of the entire process will be controlled by that of the monomolecular reaction of Step *b*. The amount of hydrazo compound undergoing cleavage will be determined by the equilibrium in Step *a* and thus by the normal potential of the reducing agent. In support of this mechanism we shall present the following evidence: (1) Step (*a*) is probable because the change of certain azo to hydrazo compounds can be shown to be reversible and the oxidation-reduction potential may be measured; (2) even with the "mildest" reducing agents that can bring about reduction of azo dyes four hydrogen equivalents are involved—the reduction does not stop at the hydrazo stage; (3) the rate of the irreversible reduction of azo dyes is essentially independent of the total concentration of reactants; (4) the relative rates of reduction by two different reagents are in general agreement with the calculations based on the theory.

The Reversibility of the Azo-Hydrazo System

Since there was no information in regard to the reversibility of the azo-hydrazo system when this work was started, we investigated the potential of the azobenzenedisulfonate—hydrazobenzenedisulfonate[3] system and obtained satisfactory evidence of the reversibility. Biilmann's study of the potential of two different amino derivatives of azobenzene appeared when our work was nearly complete and afforded still more convincing evidence of the reversibility of the process of reducing azo compounds to hydrazo compounds. His results[4] were obained in dilute acid solution by the method of mixtures; because of the rearrangement of these particular hydrazo compounds, Biilmann extrapolated to zero time in order to determine the true potential.

Our results with the disulfonate were obtained by the method of mixtures, the solvent being 0.2 *N* aqueous hydrochloric acid and the total concentration of organic material 0.003 *M;* a saturated potassium chloride bridge connected the cell with a saturated calomel electrode of known potential. As the hydrazo compound in solution is very sensitive to oxidation by oxygen, it was added to the solution in an atmosphere of nitrogen and the usual precautions were observed for eliminating all traces of oxygen. Since hydrazobenzenedisulfonate does not rearrange in 0.2 *N* hydrochloric acid, the potentials were constant after equilibrium was once established. This process, however, required one-half to three hours and only platinized electrodes gave consistent results. The relative amounts of azo and hydrazo compounds were varied from 1:9 to 9:1. The observed potentials were converted to the hydrogen scale (the liquid-junction potential being

[3] The potassium salts were employed; throughout this work sodium or potassium salts of the sulfonic acids mentioned were used.

[4] Biilmann and Blom, *J. Chem. Soc.*, **125**, 1719 (1924).

considered negligible) and the value of E_0' (the normal potential in 0.2 N hydrochloric acid) calculated from Equation 1.[5] The values are summarized in Table I, and it is evident that the agreement is satisfactory and establishes the reversibility of the system: the average is +0.379. Since the P_H value of 0.2 N hydrochloric acid is 0.76, the value of the normal potential at unit hydrogen-ion activity ($P_H = 0$) is obviously +0.424. For comparison, Biilmann's values for the amino compounds are also given in Table II; since he measured the potential against the hydrogen electrode in the *same solvent*, his results are the equivalent of E_0' at $P_H = 0$.

$$E_h \text{ (obs)} = E_0' - 0.0295 \log ([\text{Hydrazo}]/[\text{azo}]) \qquad (1)$$

Table I

Normal Potential of Potassium Azobenzene-4,4'-disulfonate-Potassium Hydrazobenzene-4,4'-disulfonate in 0.2 N HCl at 25°

Ratio of azo to hydrazo compound	E.m.f. observed E_c (against calomel)	E_h (hydrogen scale)	E_0' (Equation 1)
9.00	+0.170	+0.407	+0.379
4.00	+ .158	+ .395	+ .377
2.33	+ .152	+ .389	+ .378
1.50	+ .145	+ .382	+ .377
1.00	+ .142	+ .379	+ .379
0.666	+ .138	+ .375	+ .380
.429	+ .131	+ .368	+ .379
.250	+ .128	+ .365	+ .383
.111	+ .117	+ .364	+ .382
		Av.	+ .379

Table II

Normal Potentials at P_H = 0° and 25° of Certain Reversible Azo-Hydrazo Systems

Name of azo component	Potential
Potassium azobenzene-4,4'-disulfonate	+0.424
3,3'-Diamino-4,4'-dimethyl-azobenzene	+ .3673
3,3'-Diamino-azobenzene	+ .4095

The Number of Equivalents Involved in the Reduction of Azo Dyes

The failure to stop the reduction of azo dyes at the hydrazo stage might be attributed to the fact that the usual reducing agents are too powerful. It was, therefore, of interest to determine the nature of the products formed when the mildest reducing agent was employed which would cause reduction. We have done this by titrating electrometrically a solution of the completely reduced reagent (for example, leuco indigo-disulfonate) with a solution of the dye. If the reaction under these conditions stopped at the hydrazo stage, the end-point would be reached when one mole of dye per mole of reagent had been added. As a matter of fact we found in every instance that only half of a molecular proportion was required to complete the re-

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[5] The European convention in regard to sign is used in this paper.

action. The equation is, therefore, $2BH_2 + RN = NROH \longrightarrow RNH_2 + R(NH_2)OH + 2B$. As a check on the method, azobenzene-monosulfonate- and -disulfonate also were used. With these substances the molar ratio of substance to reagent was 1:1, corresponding to the well-known reduction to stable hydrazo compounds, $C_6H_5N = NC_6H_4SO_3H + BH_2 \longrightarrow C_6H_5NHNHC_6H_4SO_3H + B$.

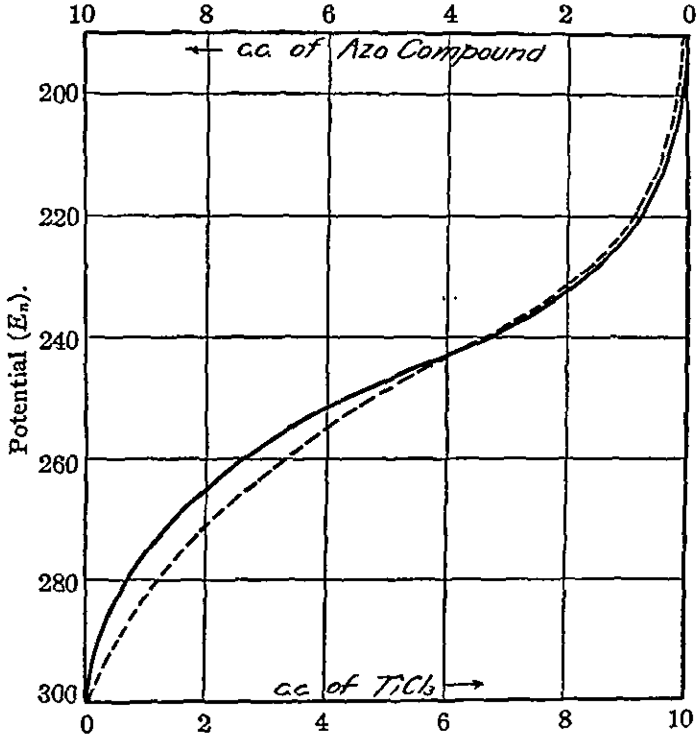


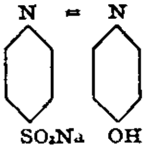
Fig. 1.—Titration of leuco indigo-sulfonate in 0.2 *N* HCl with an azo dye. The heavy line indicates the preparation of leuco compound by titration with $TiCl_3$; the dotted line represents course of titration with azo dye. The equivalent strengths of the azo solution and titanous chloride in this instance were equal.

The method is illustrated by the curves shown in Fig. 1. The heavy line shows the titration of the oxidized form of the reagent with titanous chloride; the dotted line indicates the back titration with the dye solution. The titrations were performed in the usual type of cell in the absence of air. The results are summarized in Table III. Since the end-point of the titration was not characterized by a sudden "jump" in potential, it was felt that the most accurate results would be obtained by reference to the mid-point of the titration curve rather than the end-point; this has been done as illustrated in the table. The ratio of azo compound to reagent given in Col. 7 was obtained by dividing one-half of the value given in Col. 3 by the amount of substance required for titration to the mid-point (Col. 6).

TABLE III

MOLES OF REDUCING AGENT INVOLVED IN THE REDUCTION OF HYDROXY-AZO DYES AND CERTAIN OTHER AZO COMPOUNDS

(All experiments were with 0.2 *N* HCl as a solvent and at 23°)

(1) Azo Compound	(2) Reagent	(3) Reagent used, moles $\times 10^4$	(4) Azo cpd. in 100 cc. of soln., moles $\times 10^4$	(5) Azo solution to mid-point, cc.	(6) Azo cpd. to mid-point, moles $\times 10^4$	(7) Ratio of moles of azo cpd to reducing agent
	leuco indigo-disulfonate	2.8	13	4.9	0.63	1:2.2
Same	Same	5.4	27	4.8	1.3	1:2.1
Same	leuco indigo-tetrasulfonate	2.6	15	4.7	0.70	1:1.85
Azobenzene-monosulfonate	leuco indigo-disulfonate	5.0	43	5.6	2.4	1:1.05
Azobenzene-disulfonate	Same	2.8	33	4.2	1.4	1:1

The Rate of the Irreversible Reduction of the Azo Dyes

(a) **The Effect of Dilution.**—The method of following the rate of the irreversible reduction was similar to that described in the previous papers. A weighed amount of the solid azo dye was added to a solution of an equimolecular mixture of the oxidized and reduced forms of the reagent contained in the usual type of cell in an atmosphere of nitrogen. The equimolecular mixture of oxidized and reduced reagent was prepared by titrating the oxidized form of the reagent to the "mid-point" of the titration curve with titanous chloride. The cell of about 100 cc. capacity was equipped with a mechanical stirrer, a bright platinum and platinized platinum electrode and suitable tubes for introducing nitrogen and the titrating solution from a buret; the solid dye was contained in a capsule suspended above the liquid in the cell and was dropped into the solution by turning a glass rod. A saturated potassium chloride bridge connected the cell with a saturated calomel electrode. Unless otherwise stated, all measurements were made at 23° ± 2°, and the solvent was 0.2 *N* hydrochloric acid ($P_H = 0.76$). The concentrations of the reduced and oxidized forms of the reagent were 0.0010–0.0012 *M* and an amount of azo dye was introduced such that its concentration was 0.0020–0.0025 *M*. The reagents were all of such a nature that each mole contained 2 reducing equivalents; as 4 equivalents are involved in the total irreversible reduction (see above), there was a 4 to 1 excess of azo dye at the start of each experiment.

It is obvious that the rate of change of potential of the cell after the introduction of the dye will be a function of the speed of the irreversible reduction of the azo compound. Since the potential of the cell (referred to the normal hydrogen electrode) is given by Equation 2, the potential at time *t* when the fraction *S* of the reduced form of the reagent has been oxidized will be given by Equation 3, since initially $E = E_0'$ and [reduced] = [oxidized].

$$E \text{ (potential of cell)} = E_0' - 0.030 \log \left([\text{reduced}]/[\text{oxid.}]\right) \qquad (2)$$

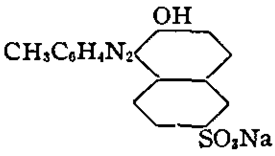
$$(E)_t = E_0' - 0.030 \log \left[(1-S)/(1+S)\right] \qquad (3)$$

The change of potential at a given time, $((E)_t - E_0')$, can thus readily be translated into the fraction of reduced reagent oxidized or the extent of the reaction at that time. (This calculation is conveniently done graphically from a curve constructed from Equation 3.)

If the irreversible reaction between the reducing agent (which we shall designate by BH_2) and the azo dye were di- or trimolecular we should expect that on diluting the solution the rate would decrease greatly (the *ratio* of BH_2 to dye being kept constant). As the results summarized in Table IV show, the rate of the process is only slightly affected by the total concentration and, indeed, in a few instances is slightly more rapid in the more dilute solution. These slight changes are undoubtedly connected with the slight changes with dilution in the value of the normal potential of the reagent (and possibly the reversible step). We have found a change from 0.001 to 0.0001 M solution with certain of the reagents to cause a change of several millivolts in the value of E_0'. Such effects are for our present purposes negligible; the rate of the irreversible reduction is essentially independent of dilution. We may conclude, therefore, *that some monomolecular reaction controls the rate of the entire process.* According to our hypothesis this monomolecular reaction is Step *b* of the mechanism outlined above.

TABLE IV

THE EFFECT OF DILUTION ON THE RATE OF REDUCTION OF CERTAIN AZO DYES IN 0.2 N HCl AT 23° BY CERTAIN REVERSIBLE SYSTEMS

Dye	Reagent	Total molar concn. of dye	Fraction of reduced reagent oxidized (S) in		
			10 min.	15 min.	30 min.
Orange II	Leuco indigo-tetrasulfonate	0.02	...	0.38	0.62
		.002	...	.38	.70
	Leuco indigo-disulfonate	.002	0.94	.96	...
		.0002	.96	.98	...
Same	Leuco indigo-trisulfonate	.002	.32	44	.66
		.0002	.55	.70	.85
Same	Leuco indigo-tetrasulfonate	.002	...	.20	.38
		.0002	...	.30	.45

The ratio of concentrations of oxidized and reduced forms of reagent and of dye in each experiment was 1:1.2.

(b) The Determination of Apparent Reduction Potential (A. R. P.).— In most of our experiments the potential of the electrodes was recorded

5, 15 and 30 minutes after the addition of the solid dye to the well-stirred mixture; the potentials of both electrodes were almost always within 1 millivolt of each other. Duplicate experiments with a number of different compounds showed that the change of potential with time was usually reproducible within a few millivolts. The fraction of reducing agent oxidized, S, may be calculated as explained above from the recorded change in potential, and thus the constant of the rate of the monomolecular reaction according to Equation 4 (t being in minutes).[6]

$$k = (1/t)\ 2.30 \log [1/(1-S)] \tag{4}$$

To illustrate the method a few typical results are given in Table V, but only the values of $k \times 10^2$ at 5, 15 and 30 minutes for each reagent employed with each dye are given in the complete summary (Table VI).

On the whole, the values of k calculated for the different time intervals are surprisingly consistent when one remembers that the reproducibility of the results is not greater than ±1 millivolt and a 20% reaction corresponds to only 5 mv. change. The probable significance of the decreasing values of k with time noted with many compounds will be discussed later. With certain compounds a difficulty was encountered in that after the addition of the solid dye there was an immediate change of potential of several millivolts corresponding to *oxidation* of the reagent. After this initial fall in potential, the potential then rose regularly, corresponding to the reduction. This effect was noticeable only with certain compounds and disappeared when the total concentration was diminished. It was not due to the introduction of a *solid* phase as it also occurred when a solution of the dye was added. We do not believe that this anomalous change in potential corresponded to a chemical reaction, but rather to some effect of the added component (dye) on the potential of the reagent (similar to a salt effect). To some extent this anomalous fall in potential makes the rates calculated for the 5-minute period uncertain.

TABLE V

ILLUSTRATING THE CALCULATION OF THE RATE OF THE REACTION FROM THE CHANGE IN POTENTIAL

Reagent: equimolar mixture of indigo-trisulfonate and leuco compound. Solvent: 0.2 N HCl. Temp., 23 ± 2°. Concn. of dye: 0.002 M. Concn. of reducing agent: oxidized form, 0.001 M; reduced form, 0.001 M.

Dye No. (See Table VI)	Rise in potential (mv)			Fraction of reagent oxidized (S)			$k \times 10^2$		
	5 min.	15 min.	30 min	5 min	15 min.	30 min.	5 min.	15 min.	30 min.
24	2	11	23	0.08	0.40	0.70	1.0	3.5	4.0
20	(−2)	17	33	...	.58	.85	...	6	6
18	7	24	37	.26	.73	.90	6	9	7
16	50	95	115	.95	>.99	>.99	65	?	?

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[6] Since the experimental errors in determining S are necessarily large, only approximate calculations were made by means of a convenient nomogram.

TABLE VI

DETERMINATION OF THE A. R. P. OF CERTAIN AZO DYES IN 0.2 *N* HCl AT 23 ± 2°
(Compounds arranged in order of decreasing A. R. P.)

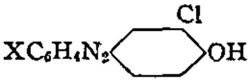
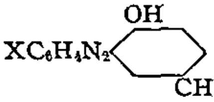
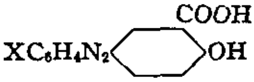
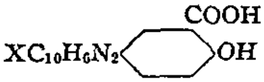
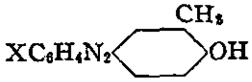
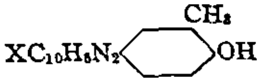
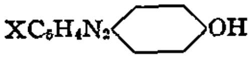
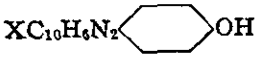
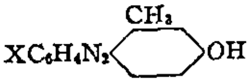
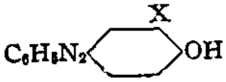
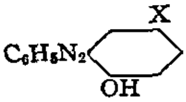
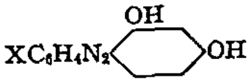
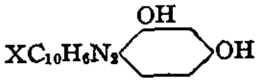
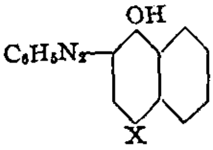
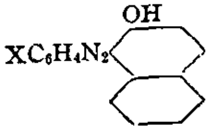
No.	Formula of Dye[a]	Reaction constant with Reagent B $(E'_0) = +0.375$ $k \times 10^2$ 5 min.	15 min.	30 min.	Reaction constant with Reagent A $(E'_0) = +0.425$ $k \times 10^2$ 5 min.	15 min.	30 min.	A. R. P. volts (H_2 electrode = 0)
1	 $XC_6H_4N_2C_6H_3(Cl)OH$	25	17	11	..	1.5	1.6	+0.435
2	 $XC_6H_4N_2C_6H_3(OH)(CH_3)$	11	8	11	..	0.8	1.5	+ .435
3	 $XC_6H_4N_2C_6H_3(COOH)OH$	11	11	7	..	.6	1.0	+ .425
4	 $XC_{10}H_6N_2C_6H_3(COOH)OH$	5	8	8	..	1.0	1.3	+ .425
5	 $XC_6H_4N_2C_6H_3(CH_3)OH$	30	21	..	..	1.0	1.0	+ .425
6	 $XC_{10}H_6N_2C_6H_3(CH_3)OH$	30	28	..	..	0.8	0.4	+ .415
7	 $XC_6H_4N_2C_6H_4OH$	16	13	11	..	1.0	.5	+ .415
8	 $XC_{10}H_6N_2C_6H_4OH$	12	10	7	..	..	.5	+ .415
9	 $XC_6H_4N_2C_6H_3(CH_3)OH$	12	10	7	..	...	<0.1	+ .410
10	 $C_6H_5N_2C_6H_3(X)OH$	7	5	4.5	..	...	< .1	+ .400
11	 $C_6H_5N_2C_6H_3(X)OH$	4.5	2.2	2.0	..	...	< .1	+ .390
12	 $XC_6H_4N_2C_6H_3(OH)OH$	3	2.5	1.8	..	...	< .1	+ .390
13	 $XC_{10}H_6N_2C_6H_3(OH)OH$	2	1.5	1.7	..	...	< .1	+ .385
		Reagent D $(E'_0) = 0.293$			Reagent C $(E'_0) = 0.325$			
14	 $C_6H_5N_2C_{10}H_5(OH)X$	>100 with Reagent E			12	9	7	+ .360
15	 $XC_6H_4N_2C_{10}H_6OH$	>100 with Reagent E			5	3	4	+ .345

TABLE VI (*Continued*)

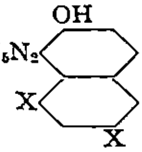
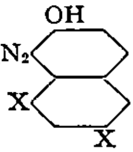
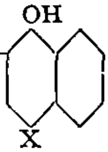
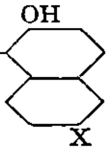
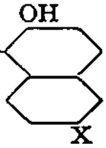
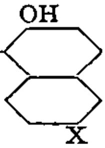
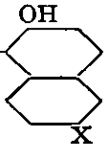
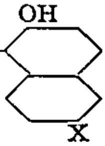
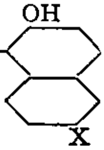
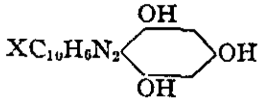
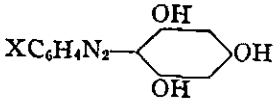
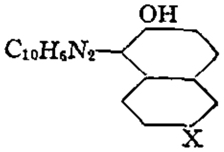
No.	Formula of Dye[a]	Reaction constant with Reagent D $(E_0')=0.293$			Reaction constant with Reagent C $(E_0')=0.325$			A. R. P. volts (H_2 electrode = 0)
		5 min.	15 min.	30 min.	5 min.	15 min.	30 min.	
16	$C_6H_5N_2$ 	65	..	..	5	3.5	4	+0.345
17	$CH_3C_6H_4N_2$ 	>100 with Reagent E			3	4	4	+ .345
18	$CH_3C_6H_4N_2$— 	6	9	7	2	3	3	+ .345
19	$C_6H_5N_2$— 	2	7	7	..	3.5	2.5	0.340
20	$CH_3C_6H_4N_2$— 	..	6	6.5	3	2.5	1.8	.335
21	$XC_{10}H_6N_2$— 	40 and 28 with Reagent E			..	1.5	1.5	.335
22	$CH_3OC_6H_4N_2$— 	..	2.5	2.0	..	1.0	1.0	.325
23	$ClC_6H_4N_2$— 	..	2.5	3.5	..	0 8	0.9	.325
		Reagent E $(E_0')=0.245$			Reagent D $(E_0')=0.293$			
24	(O)$ClC_6H_4N_2$— 	62	..	..	..	3.5	4.0	.315

TABLE VI (*Concluded*)

No	Formula of Dye[a]	Reaction constant with Reagent E (E_0') = 0.245			Reaction constant with Reagent D (E_0') = 0 293			A. R P. volts (H_2 electrode = 0)
		5 min.	15 min	30 min.	5 min.	15 min.	30 min.	
25		23	21	..	not tried			0 300
26		16	10	7	..	2.5	1.8	.305
27		10	7	7	not tried			.280

To save space the duplicate determinations made in many instances as well as the experiments with reagents where $k \times 10^2 > 100$ have been omitted as have also a number of experiments with reagents where $k \times 10^2 < 0.1$. The results of all these experiments were in perfect accord with the data given above. The following results with Reagent E were also obtained. No. 18, $k \times 10^2 = 65$; No 19, $k \times 10^2 = 65$; No 20, $k \times 10^2 = 30$; No. 21, $k \times 10^2 = 48$; No. 22, $k \times 10^2 = 50$; No. 23, $k \times 10^2 = 50$.

[a] The following abbreviations have been used in the table: X = SO_3Na; unless otherwise specified, the substituents in the benzene ring are *para* and in the naphthalene ring in the 4 position with respect to the azo linkage. The reagents employed were equimolar mixtures of the oxidized and reduced forms of the following substances: A, naphthoquinone; B, chloranilic acid; C, potassium indigo-tetrasulfonate; D, potassium indigo-trisulfonate; E, sodium indigo-disulfonate. In every case the concentrations were: leuco compound = oxidized compound = 0.001 *M*; dye = 0.002 *M* (calculated from the purity of the material as determined by titration; compare Table IX). The values for E_0' for the reagents employed were from the results published from this Laboratory and from those of Clark [*Pub. Health Reports*, **38**, 1669 (1923)].

Because of the experimental difficulties mentioned above, we have laid most weight on the values of k determined at the 15- and 30-minute periods, unless the reaction was so rapid that more than 95% had reacted at these times. In general we have not attempted to estimate the rate when the change in potential was more than 50 mv., which corresponds to about 95% reaction. Such large changes were noted only with reagents whose potentials were so far below the A. R. P. of the compound that a very rapid reaction was to have been expected.

It is convenient to define the apparent reduction potential as being the potential (E_0') of the reagent which under the specified condition will cause a 20–30% reduction in 30 minutes. This corresponds to a value of $k \times 10^2$ of 1. Such a critical reagent coincided with a reducing agent actually used in only a few instances. In all others the potential of this hypothetical reagent (and thus the A. R. P.) was calculated on the assumption that a change of potential of 40 mv. corresponded to a change of k of 10 fold;

that is, diff. pot. of reagents = 0.04 log k_1/k_2. This empirical approximation is discussed from a theoretical standpoint later. No attempt has been made to evaluate the A. R. P. more accurately than ±5 mv., and in some cases the error may be ±10 mv.

The Relative Rates of Reduction with Different Reagents

According to our hypothesis the rate of the entire irreversible reduction is controlled by the amount of hydrazo compound formed by the rapid reversible interaction of reagent and dye. From the usual electrochemical relationships we can write for this equilibrium Equation 5 (at 23°) where $(E_0')_{\text{azo}}$ is the normal potential of the hypothetical azo-hydrazo system and $(E_0')_{\text{B}}$ the normal potential of the reagent system BH_2 and B.

$$(E_0')_{\text{azo}} - (E_0')_{\text{B}} = 0.030 \log \left(\frac{[\text{hydrazo}]\ [\text{B}]}{[\text{azo}]\ [\text{BH}_2]}\right) \tag{5}$$

If we start with the following concentrations: $[\text{B}] = [\text{BH}_2] = C$ and $[\text{azo}] = 2C$ and let S be the fraction of BH_2 oxidized to B by the irreversible reduction that has taken place up to time t_1, we have the following resulting concentrations, noting that 2 moles of BH_2 per mole of azo compound are involved in the entire process: $[\text{B}] = C + CS$; $[\text{BH}_2] = C - CS$; $[\text{azo}] = 2C - 0.5\ CS$. For the equilibrium which then practically instantaneously adjusts at time t_1 we can write Equation 6a by substitution in Equation 5 and letting X be the fraction of BH_2 oxidized by virtue of *this* equilibrium and, therefore, $X(C - CS)$ the concentration of hydrazo compound formed in this instant of time by this equilibrium.

$$(E_0')_{\text{azo}} - (E_0')_{\text{B}} = 0\ 030 \log \frac{[X(C - CS)]\,[(C + CS) + X(C - CS)]}{[2C - 0.5CS - X(C - CS)]\,[(C - CS) - X(C - CS)]} \tag{6a}$$

$$\text{or} \quad (E_0')_{\text{azo}} - (E_0')_{\text{B}} = 0.030 \log \frac{X(1 - S)(1 + S + X - XS)}{(2 - 0.5S - X + XS)\,(1 - S - X + XS)} \tag{6b}$$

If X is less than 0.1 we can write an approximate equation (6c) without much error.

$$(E_0')_{\text{azo}} - (E_0')_{\text{B}} = 0.030 \log X + 0.030 \log \frac{(1 + S)}{(2 - 0.5S)} \tag{6c}$$

If we employ two different reagents of potential $(E_0')^1_{\text{B}}$ and $(E_0')^2_{\text{B}}$ and consider the value of X over the range where S is the *same* (for example, 0–50% reacted in both cases) we arrive at Equation 7.

$$(E_0')^2_{\text{B}} - (E_0')^1_{\text{B}} = 0.030 \log X_1 - 0.030 \log X_2 \tag{7}$$

Here X_1 and X_2 are the amounts of hydrazo compound formed by virtue of the reversible interaction of the reagents whose potentials are $(E_0')^1_{\text{B}}$ and $(E_0')^2_{\text{B}}$, respectively.

Since the concentration of hydrazo compound undergoing the *relatively slow* monomolecular change is $X(C - CS)$, we can write Equation 8 and, assuming X to be constant, Equation 9.

$$dc/dt = k'x(C - CS) \tag{8}$$

$$k = k'X = (2.30/t)\log(1/(1 - S)) \tag{9}$$

According to our theory the cleavage of the hydrazo compound controls the rate of the entire process; therefore, combining Equations 7 and 9 we have Equation 10. This relates the rates k_1 and k_2 with the potential $(E_0')^1_{\mathrm{B}}$ and $(E_0')^2_{\mathrm{B}}$ of the reagents employed.

$$\frac{(E_0')^2_{\mathrm{B}} - (E_0')^1_{\mathrm{B}}}{0.03} = \log\left(\frac{k_1}{k_2}\right) \tag{10}$$

From the data previously presented (Table VI) the ratios of k_1 to k_2 can be calculated for several reagents. These values of k_1/k_2 must be regarded only as approximations because of the experimental difficulties referred to. In Table VII a summary of such calculations is given; the extreme values of k_1/k_2 and the average value are recorded for comparison with the ratio calculated from Equation 10. It is evident that they are in most instances considerably smaller than the theoretical values; indeed, the empirical equation Diff. in pot. = 0.04 log k_1/k_2 used in calculating the A. R. P. is a closer representation of our average results than Equation 10.

TABLE VII

RELATIVE RATES OF REDUCTION

Reagents	$(E_0')^1_{\mathrm{B}} - (E_0')^2_{\mathrm{B}}$, volts	Range of values of k_1/k_2 Calcd (Eq. 10)	found from data given in Table VI
(A) Naphthoquinone	0.050	46	6–56
(B) Chloranilic acid			Av. 20
(C) Indigo-tetrasulfonate	.032	11	2–12
(D) Indigo-trisulfonate			Av. 4
(D) Indigo-trisulfonate	.048	40	6–15
(E) Indigo-disulfonate			Av. 9

This can be partially explained by the fact that in most instances the values of k_1 and k_2 were determined over different ranges—10–30% for the weaker reducing agent, 60–90% for the stronger. Calculations from Equation (6c) show that the value of X is not strictly constant over the whole range (as assumed in Equations 7–10) but when 80% had reacted is about one-half the value when 10–20% has. It would, therefore, be fair in most cases to double the value of k_1/k_2 found; the agreement is then somewhat better. However, even with this correction it can be claimed only that the relative rates with two reagents is of the order of magnitude of that calculated on the basis of our theory. As a first approximation to a quantitative correlation between the potentials of the reagents and the rates, we consider this satisfactory.

The extent of the reversible step must be slight even with reagents that cause fairly rapid reduction ($k \times 10^2 = 25$) because not more than a millivolt immediate change of potential takes place when the dye is introduced into the reagent. This point was tested in a few experiments in which a solution of the dye was employed and the rate noted from the first 30 seconds. We can therefore state that X is less than 0.05 with such reagents as cause rapid reduction and is less than about 0.02 when $k \times 10^2 = 1$ and $(E_0')_B$ is the apparent reduction potential. How much smaller than this X may be, we have no way of estimating. From the apparent reduction potentials given in Table VI and the assumption that $X = 0.01$, with the critical reagent, we can calculate the potential of the reversible step $[(E_0')_{azo}]$ from Equation 6c, taking S as 0.2. For the simpler substances with two benzene rings (Nos. 1–8) this gives a value for $(E_0')_{azo}$ (taking the A. R. P. as +0.425) of +0.356 at P_H 0.76 or E_0^0 (normal hydrogen ion) = +0.401. A comparison with the values of the known azo-hydrazo system (Table II) shows that this is a very reasonable value. On the same basis from Equation 9, k', the constant for the decomposition of the hydrazo compound, would be about 1, which corresponds to a half life of about 40 seconds.

The experiments we have performed differ in one respect from the usual procedure for reducing an organic substance. To increase the accuracy of the method we have employed a considerable excess of the dye; ordinarily, one employs some excess of reducing agent. In two experiments we introduced such a quantity of dye into an equimolecular mixture of reduced and oxidized reagent that the following ratios of materials were initially present: oxid.reagent: red.reagent: dye: :1:1:0.33. Since 2 molecular proportions of reagent are required in the process, when the reduction of the dye is complete under these conditions 66% of the reducing agent would be oxidized. This corresponds to a potential change of 21 mv.; therefore, the observed change of potential divided by 21 gives the extent of the reaction at the time when the potential is recorded. From this the rate of the monomolecular reaction can be calculated as usual. With indigo-tetrasulfonate and compounds Nos. 18 and 16 (Table VI), the following values of k were obtained: No. 18, $k \times 10^2 = 1.3$; No. 16, $k \times 10^2 = 1.0$. These values are to be compared with average values of 2.7 and 4, respectively, obtained by the usual procedure involving excess of dye (Table VI). It is obvious that for practical purposes the A. R. P. determined by our usual method could be employed for predicting the action of an excess of a reagent without much error. An equation similar to 6c can be easily derived for this case, and it can be calculated that the reaction constant should be about one-fifth of that observed with the excess of dye. This calculated change ($^1/_5$) is of the same order of magnitude as the change we have found ($^1/_2$ to $^1/_4$).

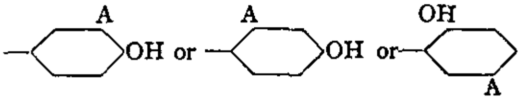
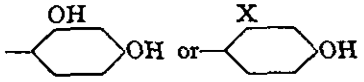
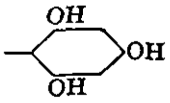
The Relation between Structure and A. R. P.

One definite generalization concerning the relation between structure and A. R. P. can be made on the basis of the data given in Table VI. *The structure of the aromatic nucleus carrying the hydroxyl group is the de-*

termining factor. Slight variations in A. R. P. are found with variation in the other aromatic nucleus (the one written on the left) but with a few exceptions these are not much greater than the experimental uncertainty (±5 mv.). Thus the following pairs of substances are similar in regard to the nucleus carrying the OH group but otherwise differ considerably, yet their respective A. R. P.s are within 10 mv. of each other: Nos. 3, 4; 5, 6; 7, 8; 12, 13; 16, 17; 20, 21; 25, 26. The greatest influence of substituents in the other nucleus is 25 mv. between compounds 19 and 24; this appears to be due to the introduction of a chlorine atom in the *ortho* position. The series, Nos. 19–24, show slight but probably definite changes that indicate an effect of substituents in this non-hydroxyl ring but this is clearly a second-order effect. The same predominant influence of the ring carrying the hydroxyl group is seen in the fact that the 27 compounds may be divided into the following groups *solely on the basis of the structure of this nucleus.*

Table VIII

Relation of A. R. P. to Structure

Compounds falling in class	A. R. P.	Structure of nucleus carrying OH group
I Nos. 1–9	+0.435−0.410	 A *not* SO_3H or OH
II Nos. 10–13	+ .400− .385	 X = SO_3H
III Nos. 14–24	+ .360− .315	Naphthalene ring with or without SO_3H groups; coupled α or β
IV Nos. 25–26	+ .300− .305	

It is particularly striking that all the compounds having the hydroxyl group on a naphthalene ring fall in Class III, although all the other classes include compounds containing the sulfonated or unsulfonated naphthalene nucleus as the *other* aromatic group.

This rather surprising effect of the group R′ in the general formula RN = NR′OH finds a ready explanation in terms of our hypothesis. The decomposition of the hydrazo compound according to our view involves the elimination of a hydrogen atom from the hydroxyl group together with the group RNH– and therefore it would be expected that the nature of R′ would be very influential in determining the rate of this reaction (k',

$$\boxed{RNH}\boxed{NHR'O}\boxed{H} \longrightarrow RNH_2 + R'\begin{matrix}\diagup O \\ \diagdown NH\end{matrix}$$

Equations 8 and 9) and therefore, the A. R. P. According to this view, the *chief cause* of the difference between the compounds would be in the value of k.' Of course, the nature of *both* rings would be expected to change to some extent the potential of the reversible step, but this might well be of secondary importance in determining the final rate. It should be pointed out that if the hydroxyl (or amino) group is in the *meta* position the elimination reaction cannot proceed and such compounds (which we have not included in this study) yield relatively stable hydrazo compounds.

Some difficulty is encountered in applying our mechanism to the reduction with cleavage of azo compounds containing the group $-OR$ or $-NR_2$ in the *para* position. We have evidence that under certain conditions such compounds may be reduced to stable hydrazo compounds. We hope to deal in a later paper with this aspect of the problem as well as a further study of the effect of hydrogen-ion concentration, and temperature.

Experimental Part

Preparation and Analysis of Dyes.—The dyes were all prepared by the usual procedure of diazotization and coupling in aqueous solution. In most cases the coupling was accomplished by adding the diazonium salt solution to a solution of the naphthol or phenol in the equivalent amount of sodium hydroxide and one molecular proportion of sodium carbonate. Special procedures were used for regulating the alkalinity in the coupling of phloroglucinol with sulfanilic acid and in coupling with phenol. The dye was salted out with sodium chloride, separated by centrifuging, washed thrice with small amounts of water in the centrifuge cups and finally sucked as dry as possible on a Büchner funnel. Wherever possible, the compounds were further purified by recrystallization from 75% alcohol; this was done with the compounds marked in Table IX with (R). All the compounds were powdered, dried for three hours at 110° and kept in a vacuum desiccator over sulfuric acid.

Great pains were taken in the purification of all the intermediates used in the preparation of these dyes as it was felt that this would give the best assurance that the resulting dyes would be homogeneous. Where possible the intermediates were purified by fractional distillation at atmospheric pressure or at 20 mm. The sulfonated compounds were purified by repeated recrystallization or, in certain cases, through the special procedure recommended for the purpose (for example, *N* and *W* salt through the zinc salt).

As a result of all these precautions we felt confident that the dyes contained very little organic impurity; the presence of a certain amount of inorganic salt is practically unavoidable. The purity of each dye in terms of its oxidizing power was determined by titration in warm solution with titanous chloride in the usual manner, the disappearance of color being taken as the end-point. The titanous chloride was standardized against iron, and a sample of Orange II purified by repeated crystallization was found to be 99.7% pure on this basis. In calculating the results of these titrations it was assumed that the material that did not oxidize titanous chloride was inert inorganic salt and the only substance involved in the titration reaction was the dye in question.

The following table lists the dyes according to the number used to designate them in Table VI, the components used in preparing them and the purity as determined by titration. In calculating the amount of dye to be used in the experiments recorded in this paper, the values for the purity given in this table were employed; it was assumed that the rest of the material was inert inorganic salts.

TABLE IX

SHOWING THE MODE OF PREPARATION AND THE PURITY OF DYES

Compound No. (See Table VI)	Components (RNH$_2$ diazotized and coupled with ROH)	Purity as determined by TiCl$_3$, %
1	Sulfanilic acid + *o*-chlorophenol	(R) 98.0
2	Sulfanilic acid + *p*-cresol	(R) 95.3
3	Sulfanilic acid + salicylic acid	75.0
4	Naphthionic acid + salicylic acid	60.6
5	Sulfanilic acid + *o*-cresol	(R) 98.6
6	Naphthionic acid + *o*-cresol	(R) 88.8
7	Sulfanilic acid + phenol	(R) 99.5*
8	Naphthionic acid + phenol	(R) 92.4
9	Sulfanilic acid + *m*-cresol	(R) 97.2
10	Aniline + sodium-*o*-phenolsulfonate	82.4
11	Aniline + sodium-*p*-phenolsulfonate	86.4
12	*Sulfanilic* acid + *resorcinol*	(R) 99.6*
13	Naphthionic acid + resorcinol	78.3
14	Aniline + Nevile and Winther's salt	90.1
15	Sulfanilic acid + naphthol	(R) 99.7
16	Aniline + G salt	(R) 87.5
17	*p*-Toluidine + G salt	(R) 94.2
18	*p*-Toluidine + Nevile and Winther's salt	88.3
19	Aniline + Schaeffer's salt	95.0
20	*p*-Toluidine + Schaeffer's salt	90.2
21	Naphthionic acid + Schaeffer's salt	79.9
22	*p*-Anisidine + Schaeffer's salt	(R) 95.8
23	*p*-Chloro-aniline + Schaeffer's salt	73.8
24	*o*-Chloro-aniline + Schaeffer's salt	88.7
25	Naphthionic acid + phloroglucinol	96.5
26	Sulfanilic acid + phloroglucinol	83.0
27	*α*-Naphthylamine + Schaeffer's salt	79.2

The compounds which it was possible to purify further by recrystallization are indicated by the sign (R). The anhydrous dye obtained by drying at 110° for several hours was analyzed except in two cases indicated by an asterisk, where hydrated material was titrated, water of crystallization determined and the results were expressed in terms of anhydrous substances.

Summary

1. The oxidation-reduction potential of the system azobenzene-disulfonate–hydrazobenzene–disulfonate has been measured in 0.2 *N* hydrochloric acid. The system is strictly reversible and the usual electrochemical equations are applicable.
2. The rate of *irreversible* reduction of certain azo dyes has been found to be essentially independent of the dilution, indicating that the rate-controlling step is a monomolecular reaction.
3. The reduction of the type of azo dye studied (*ortho*- or *para*-hydroxy-azo compound) involves complete cleavage of the molecule even with very "mild" reducing agents. The potential of the reagent and *not* the specific nature of the reagent determines the speed of this irreversible reduction.
4. The apparent reduction potentials (A. R. P.) of 27 carefully prepared and purified hydroxy-azo dyes have been measured at 23° in 0.2 *N* hydrochloric acid. The nature of the aromatic nucleus carrying the hydroxyl group seems to be the most important factor in determining the A. R. P. No exception to the validity of the electrochemical formulation of *this type of irreversible reduction* has been found.
5. A mechanism has been suggested that is in accord with all the qualitative information available. Certain approximate equations based on this mechanism lead to values for the relative rates of reduction with two reagents that are of the same order of magnitude as those found experimentally.

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NOTE

Benzohydrylamine from Benzophenone Oxime.—This year, for at least the fourth time,[1] it was reported that benzophenone oxime may be reduced to benzohydrylamine by sodium and alcohol. The other three accounts in chronological order are given by Noyes,[2] by Konowalow[3] and by Jones and Hurd.[4]

Beilstein fails to mention the preparation of benzohydrylamine by this method. Undoubtedly, therefore, when it is again needed in an investigation, this method of preparation will again be "rediscovered" and reported in the literature. Quite independently about four years ago, the author learned of Professor Noyes' priority. When approached about it at that time, Dr. Noyes graciously waved aside the suggestion that the omission of reference to his article be rectified in a Note. It is now sub-

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[1] Billon, *Compt. rend.*, **182**, 470 (1926).

[2] Noyes, *Am. Chem. J.*, **15**, 545 (1893).

[3] Konowalow, *Chem. Zentr.*, **72**, 1002 (1901).

[4] Jones and Hurd, THIS JOURNAL, **43**, 2438 (1921).

mitted, however, in the hope that others will not continue to make the same error.

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NEW BOOKS

A Condensed Collection of Thermodynamic Formulas. By P. W. Bridgman, Professor of Physics in Harvard University. Harvard University Press, Cambridge, 1925. Humphrey Milford, Oxford University Press, London. 34 pp. 24 × 16 cm Price $1.50.

The ten quantities commonly employed in thermodynamic argument, namely, p, t, v, s, dQ, dW, E, H, Z and Ψ (defined in Table I), give rise to 720 first derivatives of the type $[\partial x_1/\partial x_2]_{x_3}$, of which any three are independent, and among which more than ten billion relations exist. Any one of these relations could be obtained at once from a table giving each of the 720 derivatives in terms of the same set of three, but a much smaller table will suffice. The smallest would be one of eight entries, giving the total differentials of eight of the quantities with respect to two of them selected as independent variables, but its use would involve algebraic elimination of the ratio of the two independent differentials by means of the equation $dx_3 = 0$. Professor Bridgman's Table II (t and p independent) which is based on the relation $[\partial x_1/\partial x_2]_{x_3} \equiv [\partial x_1/\partial a_1]_{x_3}/[\partial x_2/\partial a_1]_{x_3}$, enables any one of the 720 to be written down at once; it contains 90 entries of which 45 are duplicates, double entry being employed to facilitate reference.

The 65,000 second derivatives can be obtained by purely formal differentiation from the 21 entries of Table III (t and p independent). Table IV gives the first derivatives for systems such as water in equilibrium with steam, where p is a function of t; v and t are here chosen as independent variables. Then come eight "examples of the use of the tables"—problems not at all of the conventional type; and finally a section on the extension of the tables to systems in which pressure is not the only mechanical variable, with examples involving sudden tension of steel, electromotive force and surface tension.

In the Introduction, the method of constructing the tables is made clear; the effect of the whole book on the student should be to convince him that the mathematical relations which take up so much space in conventional textbooks of thermodynamics can all be obtained "in an entirely routine way, without any tricks of manipulation," and that the real thermodynamic difficulties are those involved in clearly understanding what the problem is, and in expressing it in the language of the mathematical theory.

W. Lash Miller

Structure et Activité chimiques. (Structure and Chemical Activity.) Vol. II. Reports and Discussions of the second Conseil de Chimie, held at Brussels, April 16–24, 1925, under the auspices of the Solvay International Institute of Chemistry. Gauthier-Villars and Company, 55, Quai des Grands-Augustins, Paris, 1926. xiv + 672 pp. Illustrated. 25.5 × 16.5 cm. Price, unbound, 96 francs and foreign postage 4 fr. 25.

This report of the papers presented at the second Conseil de Chimie, of the Solvay International Institute of Chemistry, held at Brussels, April 16–24, 1925, also contains a record of the discussion of these papers.

The papers were subdivided into four groups, as follows: I. Surface Tension: The Spreading of Liquids on Water and on Solids, by W. B. Hardy. II. Crystalline Structure and X-rays: Organic Crystals, by W. H. Bragg; The Analysis of Crystalline Structures by X-rays. Agreement with Chemical Constitution, by W. L. Bragg; Structure of Colloidal Matter in the Solid State, by J. Duclaux. III. Chemical Activity: The Mechanism of Chemical Transformation, by Thomas, Martin and Lowry; The Indirect Interatomic Relations in Organic Compounds, by Frédéric Swarts. IV. Reactivity of Molecules: The Influences Exerted by Atoms or Groups of Atoms on the Reactivity of Molecules and on the Rigidity of the Bonds within the Molecules, by Tiffeneau and Orékhoff; Light and Chemical Reactions, by Jean Perrin; The Intermediate Reactions of Catalysis, by M. A. Job; Developments Resulting from the Theory of Catalytic Phenomena in Heterogeneous Reactions, by Eric K. Rideal; Catalyses by Solid Surfaces, by E. F. Armstrong and P. Hilditch; Autooxidation and Catalytic Phenomena, by Moureu and Dufraisse; Catalysis and Oxidation, by H. E. Armstrong; Absorption in Relation to Catalysis and the Actions of Enzymes, by J. Duclaux; A Survey of the Role of Catalysis in Enzymatic Reactions, by Hans von Euler.

ARTHUR B. LAMB

Gerlands Beiträge zur Geophysik. (Gerland's Contributions to Geophysics.) Edited by VICTOR CONRAD. Akademische Verlagsgesellschaft m. b. H., Markgrafenstr. 4, Leipzig, 1926. Band XV, Heft 1. iii + 89 pp. 20 figs. 23.5 × 15 cm.

Geophysicists and geochemists will welcome the reappearance of this standard periodical. Founded by the late Georg Gerland at Strassburg in 1887, it has long been a recognized repository for geophysical data, particularly in seismology. After Gerland's death it was continued by Rudolph and Hecker, until difficulties due to the War and to the cession of Alsace to France forced its suspension in 1918, after the publication of 14 regular and 3 supplementary volumes.

In the succeeding interval several geophysical periodicals have sprung up: the *Zeitschrift für Geophysik* in 1924, publishing short articles only; the *Zeitschrift für angewandte Geophysik* in 1922, whose continuance, after the completion of one volume, is said to be in doubt; and the *Geophysical Supplement to the Monthly Notices of the Royal Astronomical Society*, in 1922. Mention should also be made of the revival in 1925 of *Chemie der Erde*, which had completed one volume before the War.

The *Beiträge* now resumes publication with Volume 15 (1926), under the editorship of V. Conrad of Vienna. Its broadness of field is maintained by the inclusion, in this first number, of articles in meteorology, terrestrial magnetism, atmospheric electricity, geochemistry, seismology and oceanography. Its international character is continued through contributions from Sweden, England, Switzerland, Norway, Germany, Italy and Russia. Dr. Cottrell, Professor Noyes, and others whose hearts are in the revival of international good feeling, will be pleased to note not only the publication of articles in English, French and German, but also the addition of a supplement giving abstracts of all of them in Esperanto. As geophysics is the international science par excellence, it is fitting that a geophysical periodical should set this good example.

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Crystalline Form and Chemical Constitution. By A. E. H. TUTTON, D.Sc. Macmillan and Co., Limited, St. Martin's Street, London, 1926. xii + 252 pp. 72 figs. 22.5 × 15 cm. Price $3.60.

This book is largely an account of the researches of Dr. A. E. H. Tutton on the variation of the crystallographic and physical properties in certain isomorphous series. Essaying to answer the question as to whether "isomorphism" signifies actual equality or only close approximation of corresponding interfacial angles, he studied in great detail and with a high degree of precision the properties of the members of two such series, the alkali sulfates and selenates, and the hexahydrated double sulfates and selenates of uni- and bivalent metals. The results established, beyond any further possibility of doubt, that the angles of isomorphous substances do differ systematically, and the quality of his work is deserving of high praise. The method of presentation seems, however, somewhat unfortunate, as the following quotation from pages 51–52 will illustrate.

> "......Now no apparatus was available for preparing these plates and prisms, with truly plane surfaces exactly orientated with respect to the crystal symmetry. Hence the author caused an instrument to be constructed by Messrs. Troughton and Simms for the purpose, the 'Cutting and Grinding Goniometer,'......Prof. [Lt. Col.] F. E. Wright has recently described one in America which is practically on the lines of the author's instrument, but not so convenient. Less ambitious but useful pieces of apparatus, in many parts, for grinding surfaces on crystals, have also been devised by Wülfing and by Thomas, the last mentioned being much the more efficient, although, of course, not nearly so convenient or accurate as the author's Cutting and Grinding Goniometer."

Besides descriptions of the author's own work, the book contains brief chapters on the main facts of crystallography, parallel growths of crystals, polymorphism and similar phenomena, relations between crystal structure and optical activity, liquid crystals, and Fedorov's crystallochemical analysis. There is a bibliography, but as may be surmised from what has been stated above, it includes only articles by A. E. H. Tutton.

The author is very conservative in some respects, and seems unable to evaluate properly the significance of various modern advances in crystallography. Thus, he spends a page (229) deprecating the two-circle method of crystal measurement, holding it incapable of accuracy and difficult of application, whereas the consensus of opinion among present-day crystallographers is that the accuracy attainable by this method is quite equal to the constancy of angles usually encountered among different crystals of the same substance, and that the corresponding methods of calculation and interpretation of crystals are in every respect superior to those used in the one-circle method. On the other hand, he accepts certain inferences from x-ray studies of quartz, tartaric acid, etc., as demonstrating the atomic arrangement in these light-rotating crystals, whereas some other crystallographers see in the results presented thus far only plausible guesses.

It should not be inferred, however, that the reviewer is claiming the book to be of no interest to anyone outside the author's circle of friends or disciples. The average chemist finds most modern books on crystallography and crystal structure rather difficult reading, and so may welcome the elementary treatments of these subjects it contains.

EDGAR T. WHERRY

Einführung in die physikalische Chemie und Kolloidchemie, ins besondere für Biologen und Mediziner. (Introduction to Physical and Colloid Chemistry, Especially for Students of Biology and Medicine.) By Dr. H. R. KRUYT, Professor at the University of Utrecht. Translated into German from the second Dutch edition, by Dr. A NOWAK, Ludwigshafen. Akademische Verlagsgesellschaft m. b. H., Leipzig, Markgrafenstr. 4, Germany, 1926. xiii + 208 pp. 67 figs. 22 × 15 cm. Price, unbound, M. 8.40; $2.00; bound, M. 10; $2.40

The parts of physical chemistry of most direct application in biology and medicine are here presented in a very elementary but very clear and accurate way. The author relies mainly upon the simple kinetic theory to develop very distinct mental pictures of the phenomena he discusses. His expositions can scarcely fail to add greatly to the grasp of his nonchemical readers.

A few suggestions of possible improvement occur. For example, in the theory of lyophilic colloids the electrical effects are over-emphasized and those due to "solvation" in its various ramifications are not sufficiently discussed. In the chapter on electrical conductance the dependence of the mobility of ions upon their concentration is not mentioned, and the anomaly of strong electrolytes is left a mystery. The use of the conception of solution pressures of ions (and particularly the calculation of these quantities from single potentials) mars the discussion of electromotive force. Perrin's chance check in the calculation of the heat of decomposition of ozone from absorption spectra should not be used in substantiation of the radiation theory of reaction rate. Finally, the discussion of the "glass electrode," p. 199, might be omitted without loss from any standpoint.

E. D. EASTMAN

Reports of the Imperial Industrial Research Institute, Osaka, Japan. Dispersoidological Investigations. IV. Dispergation and Aggregation, in General, and Particularly in their Application to Cellulose, by Professor Dr. P. P. VON WEIMARN. V. Quantitative Study on Cellulose Dispergation in Aqueous Solutions of Calcium Thiocyanate Saturated at Room Temperatures and at 50°, by Professor Dr. P. P. VON WEIMARN and Dr. S. OTSUKA. Imperial Industrial Research Institute, Department of Agriculture and Commerce, March, 1925. 208 pp. 58 figs. 26 × 19 cm.

The title does not do justice to Professor von Weimarn's interesting report which, in addition to containing a wealth of experimental data on the dispersion and swelling of cellulose and its ultramicroscopic examination, outlines his general views on aggregation and dispersion (or dispergation, as he calls it), as well as his method of producing colloids by grinding and an abstract of his patents on the treatment of cellulose. Incidentally he stresses the importance of adsorption of impurities at the surfaces of ultramicroscopic crystals, which may easily amount to 10% of the whole crystal mass, and shows how such contaminated crystals may, *if we only wait long enough,* purify themselves by extruding the impurity as one large crystal lattice is formed; for on aging, "contiguity" leads to "congresence." When lyophilic groups drag others into solution, he calls the process "dispersoidal parasitism;" and he sees no need of treating adsorption "as a process of formation of a *unimolecular* layer as, for example, accepted by I. Langmuir, but merely as 'solution' in a *very thin,* superficial layer," in which he agrees with Gouy, Hardy and others. Atoms once in combination, have altered their physicochemical properties to only a certain extent because of juxtaposition; and molecules must be regarded in this light. "The more completely and perfectly satisfaction has been granted to the tendency of matter to fill up space vectorially in a given formation, the more stable is the formation"..."Among contemporary dispersoidologists, the most give in their adherence to the view that the primary cause of the aggregative activity of electrolytes consists in their neutralizing the electric charge on the superficial layers of the dispersed particles. Contrary to that view, I maintain that the electric properties of the surfaces are the consequences of the chemical condition of the superficial layer of the particles, that they are consequences of the atomic (in the wide sense of the term) processes that work themselves out in this superficial layer." We are cautioned against accepting the classical "chemical formulas" for cellulose, which is represented as containing ultramicroscopic crystals oriented into elongated strings (somewhat like the nematic substances of Friedel) but separated by adsorbed material. Viscose shows no evidence of orientation. Cellulose dispersed with the aid of calcium thiocyanate can yield a thread somewhat like viscose. An outline is given of future work planned.

The book shows vestiges of the fact that it was written (probably) in Russian and translated into English (possibly by a Japanese); but the language, though at times unusual, is comprehensible, despite Professor von Weimarn's adherence to a rather personal nomenclature.

Jerome Alexander

Chemie der freien Radikale. Entwicklungsgang und gegenwärtiger Zustand der Lehre von den freien Radikalen. (Chemistry of Free Radicals. Development and Present Status of the Subject of Free Radicals.) By Dr. Paul Walden, Professor at the University, Rostock. S. Hirzel, Leipzig, 1924. xiii + 351 pp. 21 figs. 22 × 14.5 cm.

Since the publication of Schmidlin's "Das Triphenylmethyl" twelve years ago, many new types of free radicals have been discovered. The discussion of all these extraordinarily interesting substances involves a consideration of widely different portions of organic chemistry, inorganic chemistry and physical chemistry. While the peculiar behavior of hexaphenylethane was thus appropriately enough the central theme of the first monograph on free radicals, the author of the present volume was confronted with a broader field and has taken full advantage of the widened horizon. Indeed, the book is written primarily in the spirit of one interested in those general theoretical problems which are for the most part still unsolved. A detailed presentation and discussion of many of the more strictly chemical aspects of the subject have been omitted and the emphasis has been placed on the physicochemical interpretation of the available data. The book is in this respect an excellent supplement to Schmidlin's volume and presents for the first time a critical survey of the limitations of the cryoscopic methods of determining the degree of dissociation of substances like hexaphenylethane.

The subject matter has been carefully brought up to date. The many tabulations with ample references to the literature will be of great value to all those who desire to have a complete bibliography of this field. In this way the monograph serves the investigator as well as giving to the more general reader an interesting and stimulating account of the broad outlines of the entire field.

James B. Conant

Handbuch der biologischen Arbeitsmethoden. Unter Mitarbeitung von über 600 bedeutenden Fachmännern. (Handbook of Biological Laboratory Methods; with the Collaboration of more than 600 Prominent Authorities.) Herausgegeben von Geh. Med.-Rat Prof. Dr. EMIL ABDERHALDEN. Abt. I, Chemische Methoden, Teil 1. xxiv + 926 pp. Urban und Schwartzenberg, Berlin und Wien, 1926.

This is the first part of the first division of the monumental work edited by Professor Abderhalden. The second part of the same division was reviewed in THIS JOURNAL, **48,** 539 (1926).

This part of the first division consists of four "Lieferungen," issued at considerable intervals, some of them, evidently, a number of years ago. Each is sold separately.

Lieferung 6, 148 pp., price M. 4.35, "Preparation of the Most Important Inorganic and Organic Reagents," by Krämer and Schrader, includes directions for the preparation of 88 inorganic and 107 organic substances. Very few references to the literature are given and one gets the impression from the fact that the latest given seems to be in 1911, that this portion of the book was written 15 years ago. The compilation will be found very useful and might be used by students in preparative laboratory work, but not all of the directions are carefully given. Under nitrosyl chloride the direction is given to prepare lead chamber crystals by passing nitric oxide(!) into 100% sulfuric acid, the nitric oxide to be prepared by the action of nitric acid on copper. The preparation will succeed if sufficiently strong nitric acid is used, but the concentration required is not given. Under anhydrous perchloric acid, to be prepared by vacuum distillation, no mention is made of the dangerously explosive character of the compound or of the fact that a hydrated acid distils more easily and safely.

Lieferung 30, 314 pp., price M. 7.80, contains: (a) "Testing the Most Common Solutions and Reagents," by Paul Hirsch. This gives tests for 113 substances and density tables for common bases and acids, ethyl alcohol, methyl alcohol, mixtures of alcohol and ether, formaldehyde and glycerol. (b) "Work with Optically Active Carbon Compounds," by Egon Eichwald. This gives a fairly comprehensive account of the various methods of resolving racemic compounds into their active constituents; also methods of asymmetric synthesis. (c) "Methods of Investigation in the Field of Tautomerism and Desmotropy," by Julius Schmidt. This is a very good and useful monograph on our knowledge of the subject up to about 1917. It does not contain an account of Kurt Meyer's latest and most accurate methods for the determination of enol forms—but that cannot be considered the author's fault.

Lieferung 37, 80 pp., price M. 2.25, "Methods of Demonstrating and Testing for Unsaturated Compounds," by H. Bauer. Double and triple unions between carbon atoms, unsaturated nitrogen compounds of the ammonia type and those with a double union between nitrogen atoms, double unions between carbon and oxygen, double and triple unions between carbon and nitrogen and double unions between carbon and sulfur are considered, systematically, with the characteristic addition reactions of each.

Lieferung 178, xxiv + 384 pp., includes: (a) "Avoidance of Laboratory Accidents," by F. Flury, 50 pp. Directions for avoiding accidents of various kinds, for first aid and descriptions of safety devices. Something of this sort should be in the hands of all chemists and, in abbreviated form, it should be placed in the hands of students. (b) "Indicators," by E. Czapski, 30 pp. The preparation, properties, uses and hydrogen-ion concentrations at the color changes are given for 27 indicators. It would be an advantage if the author had given a brief summary of the indicators suitable for particular uses and a chart for hydrogen-ion concentrations, such as is found in Washburn's "Physical Chemistry." (c) "Characteristic Carbon-Nitrogen Condensations of Carbonyl Compounds," by Ernst Komm, 96 pp., includes condensations with hydroxylamine, hydrazine and its derivatives and derivatives of urea. (d) "Acylation," by F. Wrede, 56 pp., includes the preparation of acetyl, benzoyl and sulfonyl derivatives, acylation with isocyanates, with carbamyl chloride, chlorocarbonic ester and with a few other acid chlorides. (e) "Esterification of the Carboxyl Group," by Franz Bachér, 136 pp.; a very comprehensive and interesting description of the varied methods used for the preparation of esters.

In the book, throughout, the subjects have been treated in a very general manner and not with particular reference to biochemical uses. This, of course, very greatly increases the value for other readers and users. It contains a mine of welcome information for organic chemists. It is a useful supplement to the new edition of Beilstein, which does not contain material of this kind.

W. A. Noyes