THE MECHANISM OF CONTACT CATALYSIS

THE
MECHANISM
OF
CONTACT CATALYSIS

BY

R. H. GRIFFITH, D.P

Senior Research Chemist
The Gas Light and Coke Co.

OXFORD UNIVERSITY PRESS
1936

OXFORD UNIVERSITY PRESS
AMEN HOUSE, E.C. 4
London Edinburgh Glasgow New York
Toronto Melbourne Capetown Bombay
Calcutta Madras
HUMPHREY MILFORD
PUBLISHER TO THE UNIVERSITY

PRINTED IN GREAT BRITAIN

PREFACE

In the preparation of this book I have been greatly assisted by the criticism and advice of a number of my colleagues, particularly that of Mr. W. K. Hutchison. I am also indebted to those who have been associated with me in experimental investigations, whose names appear in the text, and to Mr. J. H. G. Plant for his help in checking references and proofs. The reproduction of many original drawings has been made possible owing to the generosity of the following societies: The Royal Society, The Chemical Society, The Faraday Society, The American Chemical Society, The Society of Chemical Industry, The Institution of Petroleum Technologists, The Institution of Gas Engineers, and the Deutsche Bunsen Gesellschaft. Additional drawings have been derived from the *Zeitschrift fur anorganische und allgemeine Chemie*, and the *Zeitschrift fur physikalische Chemie*, with the permission of the editors, and from the *Journal of Physical Chemistry*.

R. H. G.

London, March 1936.

CONTENTS

INTRODUCTION vii

ABBREVIATIONS x

I. EXPERIMENTAL METHODS 1

II. ADSORPTION 19

III. PROMOTERS AND CARRIERS 64

IV. POISONING AND RETARDATION . . . 93

V. EXAMINATION OF THE CATALYST SURFACE . 106

VI. GEOMETRY OF THE CATALYST SURFACE . 133

VII. THE MECHANISM OF CATALYSIS . . . 152

VIII. THE DEVELOPMENT OF CATALYSTS . . . 184

INDEX: AUTHORS 195

INDEX: SUBJECTS 198

INTRODUCTION

SUCH rapid advances have been made during the past ten or fifteen years in the technical development of catalytic processes, that the time appears opportune to consider what progress has been made in the theoretical treatment of the subject.

If the phenomena of catalysis had been explored completely, it should be possible not only to give a logical explanation of every known example, but also to predict the conditions under which new reactions could be carried out. Although it cannot be suggested that knowledge has reached such finality, yet there have been many important discoveries concerning the mechanism of heterogeneous catalysis, subsequent to the publication of such standard works as that by Sabatier or Rideal and Taylor's *Catalysis in Theory and Practice*, which remain scattered among a large number of scientific journals.

An attempt will therefore be made to refer to the more important of such publications relating to the study of surfaces, or to other properties of catalysts. The wide appeal of the subject, and its manifest attractions for the student and for those engaged in research, are sufficient encouragement for the compilation of the present survey. A clear sign of the vigour with which experimental work has recently been carried out is the rapid development which has taken place during the past five years.

The practical importance of catalysis has assumed such dimensions in industrial chemistry that attention has naturally been focused largely on the conditions of practical operation, and on such reactions as the synthesis of ammonia or methanol, and the hydrogenation of carbonaceous materials. At the same time it must be appreciated that many other processes are more suitable for the study of the fundamental features of catalysis. It is proposed, therefore, to discuss catalytic reactions in the light of the information they yield concerning catalysis rather than on account of their industrial importance, and no technical details of these processes will be given.

At the same time an explanation of the kinetics of catalytic reactions is not alone sufficient for the complete understanding of the principles involved, as the nature of the surface itself needs further exploration, and both lines of approach are of equal importance. The subject-matter of the different chapters is so closely related that it has not been found easy to decide on the most suitable order of treatment, but the insertion of cross references has partly eliminated this difficulty.

Accordingly, the methods used in laboratory investigation of catalytic reactions are first described, followed by an account of the study of adsorption by catalysts, and of the means available for the exploration of solid structures and surfaces. The occurrence of promoter action and the application of catalyst supports or carriers is followed by a description of poisoning and retardation.

The developments which have taken place in the study of the kinetics of catalytic reactions are then considered together with the theoretical treatment of the more special features of the subject, and finally the position is examined with regard to the prediction or selection of catalysts for any given reaction.

This order of treatment, which leaves the discussion of reaction kinetics to so late a stage, has been necessitated by the fact that the catalyst, rather than the reactants, is the main subject of study throughout the book.

An attempt has been made in each section to indicate the directions in which more information appears to be needed, and to suggest the developments which may be hoped for in the application of new knowledge to practical purposes. The treatment of the individual subjects has been made chronological as far as possible, particularly in the case of recent publications, but it will be understood that in many cases an exhaustive record of experimental data has not been attempted and that attention has been confined to typical examples.

Throughout the whole survey stress has been laid upon methods of experiment as well as on the interpretation of results, in the belief that skilful manipulation is a vital necessity in the study of catalysis, and that many of the tentative suggestions which have been made concerning the theory of heterogeneous reactions can only be proved or discarded when many more practical results are available.

A number of terms particularly associated with catalysis are employed throughout this work. In order to avoid frequent cross reference, brief definitions of these are included at this point; more detailed descriptions appear in the appropriate chapters.

Activity: the activity is a basis for comparing the efficiency of different catalysts, which may be expressed in any convenient way depending on experimental conditions. Generally, the yield of a given product or the disappearance of a reactant in unit time is chosen as a measure of activity.

Promoter: a promoter is a second component of a mixed catalyst which is present in relatively small amount, and which gives appreciably greater activity than would be anticipated on the grounds of simple additive effects.

Carrier: a carrier is an inert material which is mixed with the catalyst, and which may affect its physical properties, but does not behave as a promoter.

van der Waal's adsorption: this term is applied to the low-temperature adsorption of a gas or vapour by a solid which is completely reversible and which attains equilibrium very rapidly.

Activated adsorption takes place at a higher temperature than the van der Waal's type, and reaches equilibrium much more slowly. Its velocity is characterized by a temperature coefficient from which an apparent energy of activation can be calculated.

Chemi-sorption occurs when a gas is held by the surface in the form of a chemical compound, and is not recoverable from it by exhaustion alone.

ABBREVIATIONS

USED IN REFERENCE TO ORIGINAL PAPERS

ABBREVIATED TITLE.	JOURNAL.
Act. Physicochim.	*Acta Physicochimica U.R.S.S.*
Ann. Physik.	*Annalen der Physik.*
Ber.	*Berichte der deutschen chemischen Gesellschaft.*
B.P.	British Patent.
Bull. Inst. Phys. Chem. Res. Japan.	*Bulletin of the Institute of Physical and Chemical Research, Japan.*
Canad. J. Res.	*Canadian Journal of Research.*
Chem. and Ind.	*Chemistry and Industry.*
Chem. Zentr.	*Chemisches Zentralblatt.*
Compt. Rend.	*Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.*
F.R.B.	Fuel Research Board.
Fuel.	*Fuel in Science and Practice.*
Gas J.	*Gas Journal.*
Gazzetta.	*Gazzetta chimica italiana.*
Ger. Pat.	German Patent.
Giorn. Chem. Ind. Appl.	*Giornale di Chimica Industriale ed Applicata.*
Ind. Eng. Chem.	*Industrial and Engineering Chemistry.*
Inst. Gas Eng.	Institution of Gas Engineers.
J. Appl. Chem. Russia.	*Journal of Applied Chemistry, Russia.*
J.A.C.S.	*Journal of the American Chemical Society.*
J. Chem. Phys.	*Journal of Chemical Physics.*
J.C.S.	*Journal of the Chemical Society.*
J. Phys. Chem.	*Journal of Physical Chemistry.*
J.S.C.I.	*Journal of the Society of Chemical Industry.*
J. Scient. Inst.	*Journal of Scientific Instruments.*
Kolloid-Z.	*Kolloid-Zeitschrift.*
Naturwiss.	*Die Naturwissenschaften.*

ABBREVIATED TITLE.	JOURNAL.
Proc. Camb. Phil. Soc.	*Proceedings of the Cambridge Philosophical Society.*
Proc. Phys. Soc.	*Proceedings of the Physical Society of London.*
P.R.S.	*Proceedings of the Royal Society.*
Sci. Papers Inst. Phys. Chem. Tokyo.	*Scientific Papers of the Institute of Physical and Chemical Research, Tokyo.*
T. Farad. Soc.	*Transactions of the Faraday Society.*
Trans. VI. Mendeleev Cong. Theor. Appl. Chem.	*Transactions of the Sixth Mendeleev Congress of Theoretical and Applied Chemistry.*
Z. anorg. Chem.	*Zeitschrift fur anorganische und allgemeine Chemie.*
Z. angew. Chem.	*Zeitschrift fur angewandte Chemie.*
Z. Elektrochem.	*Zeitschrift fur Elektrochemie.*
Z. Physik.	*Zeitschrift fur Physik.*
Z. Phys. Chem.	*Zeitschrift fur physikalische Chemie.*

CHAPTER I

EXPERIMENTAL METHODS

THE definition of heterogeneous catalysis does not, of course, restrict it to the case of a gas-solid system, but the study of reactions involving these two phases has so much to recommend it, in ease of manipulation and flexibility of conditions, that it is generally preferable to the use of liquid-solid or gas-liquid systems. In technical processes three-phase systems are often important, as in the hardening of fats or in the hydrogenation of certain types of hydrocarbon oils.

Static methods.

For the study of reaction kinetics static methods are preferable, and the simplest type of apparatus is often sufficient to give a complete insight into a process; the use of a relatively inert catalyst is generally preferable to one which has a very high activity, as it enables the course of the reaction to be followed more accurately. The experimental methods of Langmuir[1] for the study of gases at very low pressures, and the later technique of Bodenstein and of Hinshelwood, exemplify the apparatus which is required in determinations of this kind.

As the catalysts necessary for this class of experiment are of the simplest type, being generally wires of platinum, gold, silver, or other metals, little need be said as to special methods of preparation. The activity of a wire can, however, be modified to a considerable extent by pre-treatment such as heating to a high temperature, or by cold working, etching, and alternations of oxidation and reduction. It is always necessary, during a lengthy series of experiments with any particular catalyst, to check the activity at intervals under standard conditions in order to be certain that drift effects, activation, or poisoning have not introduced a further variable into the determinations.

---

[1] *J.A.C.S.*, 1912–16.

Streaming methods.

In this type of experiment it is preferable to maintain the solid catalyst at a known steady temperature, and to allow the reactants to come into contact with it. Pre-heating of the gases or vapours, before they reach the catalyst, is frequently desirable in order to avoid cooling of the mass. This technique is not suitable for kinetic investigations, but is useful for comparison of catalyst activity, particularly where this is high. It does not give such reliable information as to the concentration-time curve, as the former is varying throughout the catalyst mass and the latter is not accurately determinable.

The conditions of experiment therefore resolve themselves into the passage of one or more reactants over the solid catalyst, which may take the form of a gauze or be packed in threads, pellets, or powder. Except in the case of metals such as nickel or platinum it is more usual to employ the catalyst in small lumps; these are often obtained by extruding a paste through a suitable orifice, drying the threads which are produced and breaking them into convenient lengths.

Preparation of catalysts.

The fact that it is generally desirable to prepare catalysts under carefully controlled conditions, especially avoiding high temperature, makes a precipitated material a useful starting-point, and such a substance is particularly adapted to handling in paste form. In other cases recourse must be had to very fine grinding by means of a paint mill or some similar device, in order to obtain a product which will bind satisfactorily into pellets. It is generally preferable to select a starting material which will undergo some chemical change before it is converted into the form which actually functions as the catalyst. For instance, a nickel catalyst can be prepared by the reduction of nickel hydroxide, or tungsten oxide can be obtained by dehydration of tungstic acid, and a sulphide may be produced by passing hydrogen sulphide over an oxide in granular form. The conditions under which such preliminary treatments are carried out must be very carefully controlled in order to obtain reproducible results, particularly in catalyst mixtures which contain more than one component.

In the case of platinum catalysts, for example, G. B. Taylor, Kistiakowsky, and Perry[1] found that the conditions of preparation greatly affected the size of individual crystals in the product. The substance obtained by heating ammonium chloroplatinate in hydrogen at 200°, followed by further heating in nitrogen, was a coarse crystalline powder with very low activity, while the preparations resulting from reduction of platinic chloride with hydrazine or formaldehyde, and precipitation with caustic soda, were composed of minute crystallites and had a high activity.

The temperature of precipitation of a hydroxide may also affect its activity. When copper catalysts were prepared by reduction of the precipitate obtained by adding ammonia to solutions of copper nitrate, Frohlich, Fenske, and Quiggle[2] found that a maximum activity for the decomposition of methanol resulted when the addition was carried out at 22°. If the precipitation was done with caustic soda instead of ammonia the activity at 360° was considerably higher owing to the effect of sodium hydroxide held by the precipitate, but at higher contact temperatures this substance had a harmful effect and the catalyst lost its activity.

The conditions of preparation, such as drying or grinding, may also modify the chemical composition of the catalyst before it has been in use. Middleton and Ward,[3] for example, found that precipitated nickel and cobalt sulphides always contained more sulphur than corresponded with the formula MS. If the precipitates came into contact with air before they were dried, they contained oxygen, hydrogen in amounts approaching atomic equivalence to the sulphur present, and small quantities of nitrogen were also detected. Partial oxidation, hydration, or hydrolysis of precipitates in general may be anticipated in many cases, particularly where slow drying at elevated temperatures is employed.

The shape of the particles will have an effect on the results obtained in cases when the rate of diffusion of the reactants

---

[1] *J. Phys Chem.*, 1930, 34, 748.

[2] *J A.C.S*, 1929, 51, 61, 187.

[3] *J.C.S.*, 1935, 1459.

to the catalyst surface is the factor controlling the speed of the reaction.

The size of the catalyst pellet used in the reaction vessel will depend somewhat on the conditions used, but the most desirable can be readily determined in each case. Adadurov and Gernet[1] found that the extent of conversion of sulphur dioxide to trioxide in contact with vanadium catalysts depended on the shape of the lumps and their resistance to gas flow, hemispherical pieces being preferable to those of rectangular character. It is necessary to avoid such finely divided powders that channelling occurs or that excessive back pressure is thrown on the system, or that dust is carried over by the gas stream passing through the catalyst layer. At the same time each particle should be porous and completely accessible to the reactants, anything in the nature of a hard glaze on the outside of a pellet being undesirable.

When a strongly exothermic reaction is being carried out in contact with a catalyst it is necessary to provide means for dispersing the heat evolved in order to prevent the temperature of the mass from rising too high. For this purpose Fischer and Meyer[2] have prepared metallic skeleton catalysts, used in the synthesis of hydrocarbons from carbon monoxide, which are characterized by good heat-conducting properties. Alloys of nickel or cobalt with aluminium or silicon were treated with alkali to extract the two latter components, and this left the active substance in a finely divided state.

Promoted catalysts.

The preparation of promoted catalysts needs even greater care than is required with those consisting of a single substance. It will be shown later (p. 74) that it is essential to obtain uniform distribution of the promoter, and as this is present in very much smaller quantity than the main catalyst it is not always easy to comply with this condition. The methods which are available are (1) co-precipitation from mixed solutions, (2) evaporation of mixed solutions, probably

---

[1] *J. Appl. Chem. Russ.*, 1933, **6**, 450.

[2] *Brennstoff-Chemie*, 1934, **15**, 84.

followed by heating of the residue, and (3) moistening of a powder with a solution.

1. In several cases of two-component catalysts, satisfactory results have been obtained by the precipitation of mixed hydroxides, carbonates, &c. It is, however, doubtful whether the method can be applied when very small concentrations, or particularly small changes in concentration, are being studied. Only very rarely will the conditions of ion concentration in the solution be such that both components are precipitated simultaneously and in a steady ratio. An apparently complete and uniform precipitation may in fact be very irregular and the products will always require exact analysis as a check on their composition. As an illustration of the difference which may arise in the preparation of two-component catalysts, some data of Frohlich, Fenske, and Quiggle[1] will serve. The decomposition of methanol on copper-zinc catalysts was studied under standard conditions for five different methods of preparing the mixture of 95 molar per cent. copper oxide and 5 per cent. zinc oxide. The comparative activities are shown in Table 1.

TABLE 1

Mixed catalysts obtained by alternative methods

Method of preparing catalyst	*Relative activity*
Hydroxides precipitated together	100
Hydroxide gels mixed	83
Zinc precipitated on suspended Cu hydroxide	75
Calcined mixed nitrates	70
Copper precipitated on suspended Zn hydroxide	67

2. To a smaller extent the same objections apply to the second method, as the evaporation of a mixed solution will generally lead to the separation of the major component first; there will accordingly be a larger concentration of the lesser component in the final liquid and in the solid deposited from it. Further difficulties arise when the solid thus obtained is heated to a higher temperature, as partial solution of some of the solid may occur in the water still present, and decomposition of one component may take place at a very much

---

[1] *Ind. Eng. Chem.*, 1928, 20, 694.

lower temperature than that of the other; when this is the case it may be transformed into a finely divided powder before the crystalline state of the other component is altered.

3. The remaining possibility has much to recommend it in many respects. The main component can be initially prepared in a high state of purity, and having a known composition. It can be weighed exactly, without the uncertainty introduced by incomplete precipitation, and exact amounts of the promoter can also be taken. The powdered catalyst can also be available in a large quantity of uniform grain size so that a whole series of experiments may be made with a standard material.

In order to apply this procedure with the greatest effect, a solution of the promoter is required which can moisten the catalyst powder to give a paste, but this solution must deposit its solute uniformly and irreversibly on the powder. If this condition is not fulfilled the preparation will be no more uniform than in either of the previous cases; irregularities in the relative amounts of water and solid in the paste will lead to changes in concentration of the solute, and when the paste is dried there will probably be a concentration of the solute in the last few drops of liquid.

The ideal way to overcome these difficulties is to use the promoter in colloidal solution and to coagulate the colloid before the paste is dried. In the case of addition of silica as a promoter, for example, excellent results are obtained by using colloidal solutions, adding them to a powder and warming the resulting paste until the mixture is changed to a jelly. The whole may then be dried without any risk of changing the dispersal of the promoter. If a colloidal solution is not available, it is preferable to bring about deposition of the promoter by reaction, but this method is of limited applicability; an example will be found (p. 74) in the chapter dealing with promoter action.

Purification of catalysts generally involves washing free from soluble matter in cases where they have been obtained by precipitation. This is always advisable even though many catalysts are now known which are extremely resistant to poisons of all types, the impurities may, on the contrary, function as promoters. When ammonia has been used to prepare the precipitate, thorough washing is not so essential, on account of the volatility of ammonium salts, unless the reaction to be studied is one which takes place at ordinary temperatures. Drying of the catalyst pellets is generally completed in the reaction vessel, so that there is as little disturbance of the material as possible.

Carriers.

The selection of carriers or supports is usually made from a fairly limited range of materials such as china-clay, yellow clay, bauxite, silica-gel, alumina-gel, pumice, or charcoal. Charcoal and other natural products are open to the objection that they vary considerably in character from sample to sample; the former has a variable ash content which may play an important part in catalytic changes. It is also open to the objection that re-oxidation of the catalyst, which may be necessary in technical processes, is not possible on account of the combustion of the carrier which would occur. For laboratory experiments on carrier action, therefore, some substance of known and simple chemical composition is preferable.

As to the form in which the carrier is applied, the same general principles may be followed as in the case of simple catalysts. Pieces of uniform size are required and may be prepared either by adding a solution of the catalyst compound, e.g. to charcoal or pumice, or by mixing the powdered solids mechanically and making pellets from the resulting paste.

Activity.

The primary requirement in comparative experiments with catalysts is to determine their activity in carrying out a given reaction, or else to study the kinetics of the changes involved. These two methods of approach are both capable of revealing the mechanism by which the process takes place, but the technique is generally rather different in the two cases.

Attempts to follow the kinetics of a reaction are most conveniently performed by a static type of apparatus such as that shown in Fig. 1. Here the conditions of the raw material or materials may be varied over a wide range of concentration and temperature, and the course of the reaction is followed by some means such as change in pressure. This method is particularly applicable to the simpler gas reactions and has been applied by Hinshelwood and others (see p. 153). Under certain circumstances the more tedious procedure of full analysis of the system at different stages of the reaction is necessary to follow the changes properly. The catalysts applied to this type, as mentioned previously, are simpler in character than those applied to dynamic methods and are, in fact, often chosen on account of their relatively slow action. It is also frequently possible, by choice of reactants, to obtain conditions where a given product is removed from the reaction zone as soon as it is produced; examples of this are in the decomposition of hydriodic acid where solid iodine is condensed on the cold wall of the bulb and has a negligible vapour pressure at 0°, or again in the interaction of hydrogen and carbon dioxide where water is constantly removed by the presence of a layer of strong sulphuric acid in the experimental method of Hinshelwood (see Fig. 1).

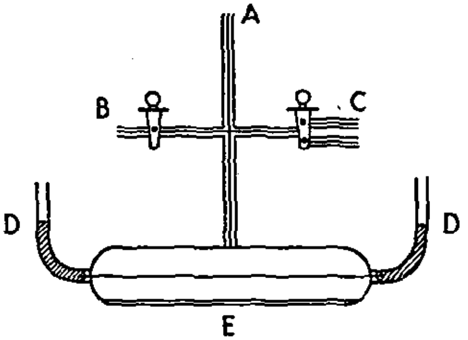


FIG. 1. Typical apparatus for static experiments.

A, connection to manometer.
B, „ pump.
C, „ gas supply.
D, *D*, leads for heating catalyst wire.
E, reaction bulb, with layer of sulphuric acid at the bottom.

Mixtures of gases of any composition can easily be fed to the bulb, and the pressure of the system can be observed by direct reading on the manometer. The temperature of the catalyst, in the form of the wire filament, can be altered by controlling the heating current passed into it, and the whole process can be interrupted instantaneously at will by shutting off the current.

In the case of dynamic experiments rather more complicated experimental methods are usually necessary, but the course of the reaction may be followed by changes in chemical or physical properties. For instance, in the decomposition of ammonia it is possible to measure the volume of permanent gas that is formed, or in the formation of benzene from mixtures of phenol and hydrogen the contraction in the volume of exit gas is a measure of the amount of reaction. Where no convenient change of volume can be determined, chemical analysis of the products is available as an alternative, but it is undoubtedly more tedious. An interesting case is presented by the change of para-hydrogen to ortho-hydrogen in contact with catalysts, where there is no change in the chemical composition and no change in volume, but the course of the reaction can be followed by determination of the thermal conductivity of the gas leaving the catalyst zone.

The same method may be applied to cases where a gaseous reaction product has a thermal conductivity widely different from that of the reactant; an example is found in the decomposition of ammonia, where Hinshelwood and Burk[1] observed that the rate of heat loss from the reaction vessel increased as the change proceeded.

A method depending on the amount of heat liberated during an exothermic reaction has been developed by Pietsch and Seuferling[2] in which the apparatus shown in Fig. 2 is employed. This consists of a silver disk to which a coil of constantan wire is fixed, and the catalyst paste is spread between the spaces on the surface. The wires *a* and *b* form the leads of the silver-constantan thermocouple, and an independent heating current can be supplied by means of the

---

[1] *J.C.S.*, 1925, **127**, 1105.

[2] *Z. phys. Chem.*, 1931, Bodenstein Festb., 523.

remaining pair of wires *c* and *d*. If the catalyst has to be used in the form of large pieces, a modified form of apparatus is available in which a silver tube is employed instead of the disk. The rise in temperature recorded by the thermocouple, under standardized conditions of gas flow over the surface, is used as a measure of the activity of the catalyst; extensive heat evolution must evidently be avoided in order to prevent the temperature rising beyond the limits set for the particular series of experiments.

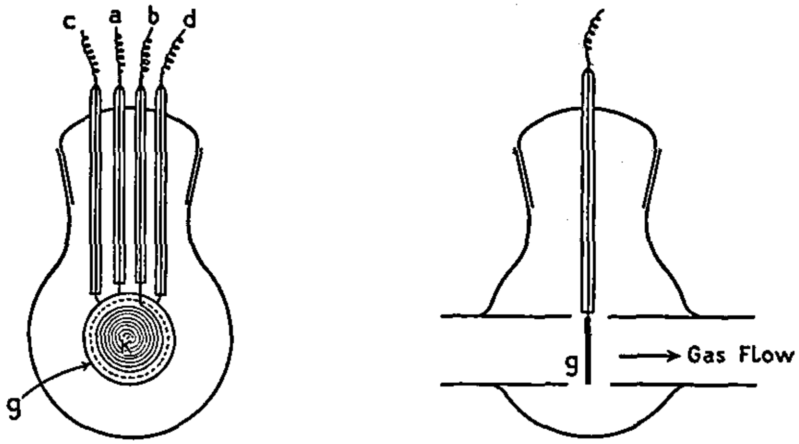


FIG. 2. Glass reaction vessel, approximately full size.
a, *b*, thermocouple.
c, *d*, heating leads.
g, silver disk.
K, constantan wire.
The catalyst is pasted between the turns of *K*.

The comparative activity of different catalysts must be determined under strictly controlled conditions, but since the dominating factor, in changes which are reasonably far removed from equilibrium conditions, is the time of contact of the reactants with the catalyst, it is preferable to express all measurements in terms of a standard volume of catalyst. This is generally done in the form of a space-time yield; that is, the yield of a product from unit volume of catalyst in unit time. This basis removes the difficulties introduced by variable or uncertain density of the catalyst, but it makes it essential that the apparent volume of the granules should always be compared at the end of an experiment. This is necessary because loss of water, or other changes leading to shrinkage, almost invariably occur during the heating of the catalyst; the extent to which this takes place varies over very wide limits, so that it is unsafe to assume that equal volumes of unused catalyst will remain equal when they have been at work for several hours.

When the volume occupied by the pellets has been determined it is possible to correct the activity figures obtained to a standard arbitrary volume provided that certain conditions are fulfilled; these are (1) that the granules are of uniform and similar size and shape, (2) that they are packed equally without distortion in the measuring vessel, (3) that powdering does not occur, (4) that the volume of catalyst used is not so small that the reacting gases fail to make efficient contact with it, (5) that channelling of the gases over the catalyst is not taking place, and (6) that complete or nearly complete conversion of the reactants would not be given by a very much smaller volume of catalysts.

These demands can be sufficiently well satisfied, within reasonable limits, particularly if the results are only required on a comparative rather than an absolute basis, but successful experiment will always depend on careful selection of conditions, such as temperature and gas velocity, which will reduce the importance of errors of this kind.

Use of the back reaction.

It is often found more convenient to study a reaction in one direction than in the reverse direction; for instance, the conditions of ammonia synthesis from hydrogen and nitrogen require high pressure in order to obtain reasonable conversion. The back reaction, however, proceeds more satisfactorily at low than at high pressure so that a simpler apparatus can be set up to study catalysis of ammonia decomposition.

This method of attack is subject to grave limitations in a great many processes of technical application owing to the intrusion of secondary reactions. In the case of methanol synthesis, for example, it has been shown that there is only a rough parallel between the catalyst activity for the forward and back reactions, as shown by the curves of Figs. 3 and 4, due to Frohlich,[1] for the synthesis and decomposition of methanol.

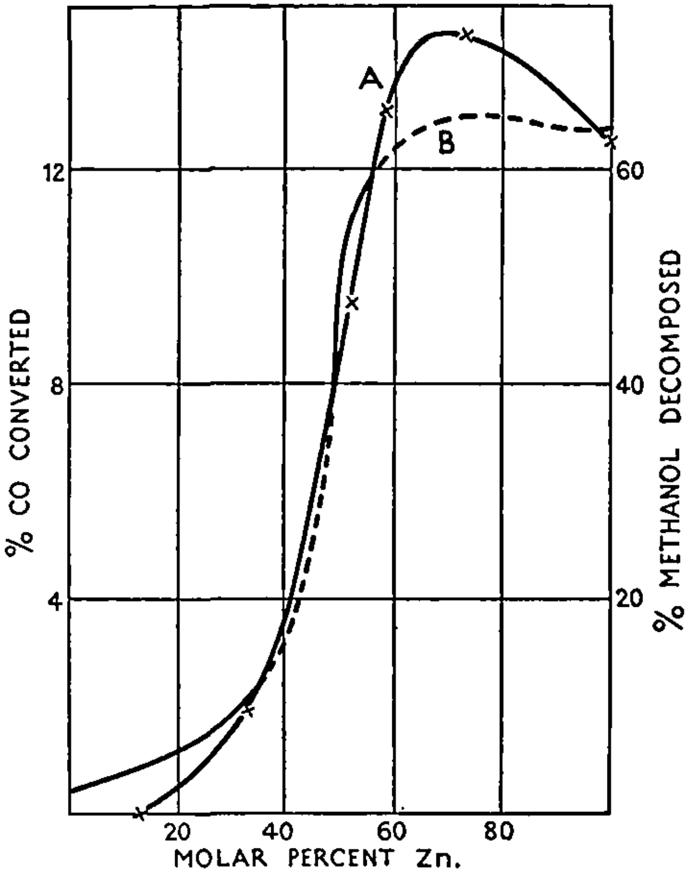


FIG. 3. Forward and back reaction with mixed catalysts, zinc oxide-copper.
A, synthesis.
B, decomposition.

In the case of processes involving hydrocarbons or other organic compounds the position becomes even more complicated and no reliance can be placed on data obtained at low pressures for drawing conclusions as to the results to be expected at high pressures.

---

[1] *Ind. Eng. Chem.*, 1928, **20**, 1327; 1929, **21**, 867.

The difficulties of direct high-pressure determination of catalyst activity are, however, largely disappearing and some very simple forms of apparatus have been devised for work of this kind. Ormandy and Burns describe equipment of this type,[1] which is illustrated in Fig. 5 and which compares favourably, as regards ease of operation, with a low-pressure catalyst system.

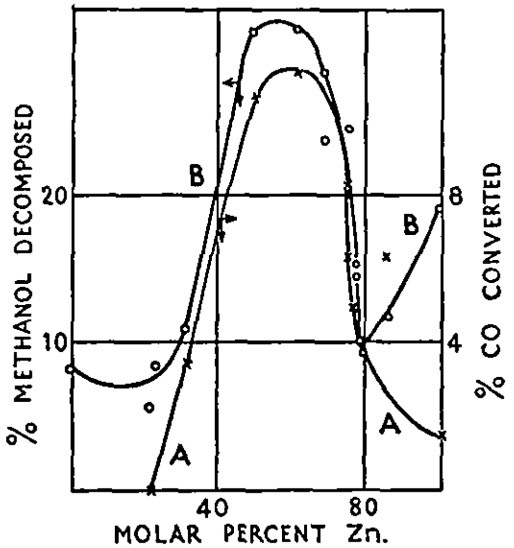


FIG. 4. Relation between synthesis and decomposition of methanol, zinc oxide-chromium oxide catalysts.

A, synthesis at 204 atm. and 340°.
B, decomposed at 1 atm. and 340°.

The raw material is drawn from a burette 1 by means of a pump 2 which forces it to the top of the reaction vessel 4 containing the catalyst at any desired temperature. Before coming into contact with the catalyst, admixture with a gas, such as hydrogen, entering at valve H_2, is carried out, the source of this gas being either a high-pressure reservoir or an independent compressor attached to the outfit. After passing over the catalyst the products are led to the condenser 6 and the separator 7, where any liquids which are formed are collected and permanent gas is allowed to escape by way of the

---

[1] World Petroleum Congress, 1933, paper 170.

valve 8. Suitable pressure gauges and valves are fitted as required, and control of the heating current to the furnace surrounding the catalyst vessel is obtained by means of a variable resistance. The rate of supply of liquid raw material can be varied by alteration of the effective pump stroke, amounts as small as 10 c.c. per hour being attainable. Although the component parts of the high-pressure system, for use at pressures up to 300 atmospheres and temperatures up to about 500°, must be made of steel, a liner of any desired material can be fitted to the catalyst vessel.

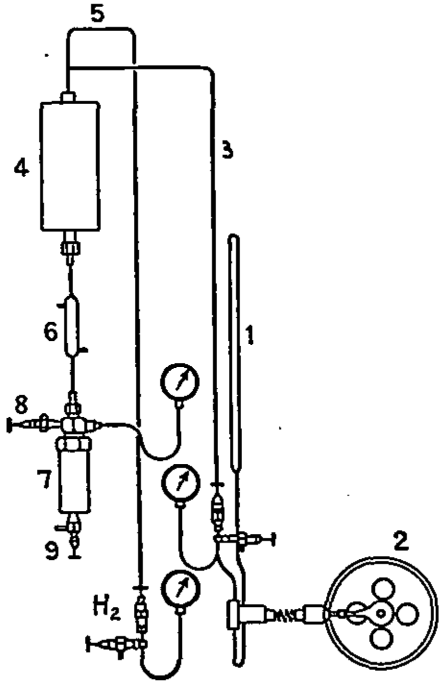


FIG. 5. Laboratory apparatus for catalytic experiments at high pressures.

1. Burette containing material under treatment.
2. Pump supplying catalyst tube via line 3.
4. Furnace containing catalyst.
5. Supply of compressed gas such as hydrogen, via valve H_2.
6. Condenser for reaction products.
7. Separator for withdrawal of liquid.
8, 9. Control valves.

This arrangement is particularly designed for reactions involving a liquid and a gas.

Factors affecting catalyst activity during use.

The activity of the catalyst will chiefly depend on its specific nature, the temperature at which it is used, and the conditions under which the raw materials are applied. No general discussion of the specific nature of the catalyst can be introduced at this point, but the effects of time and temperature can be considered in general terms. Typical time-activity curves are shown in Fig. 6; curve *A* is the more usual form in which a high initial activity decreases fairly rapidly to a steady figure, and this is maintained over very long periods. Curve *B* is similar to the former but no steady period is ever attained and a slow downward drift persists until zero activity is attained. In curve *C* the activity rises from a low value and then becomes steady over long periods. It is evident that other variations of this type, or of several types at the same time, may occur. With types *A* or *C* little difficulty arises in direct comparison of the activity of different catalysts, as the final steady value is taken, but in type *B* some rather more arbitrary unit must be chosen; for instance, the time necessary for the activity to fall to a fixed value, or alternatively the value after a fixed time, must be recorded.

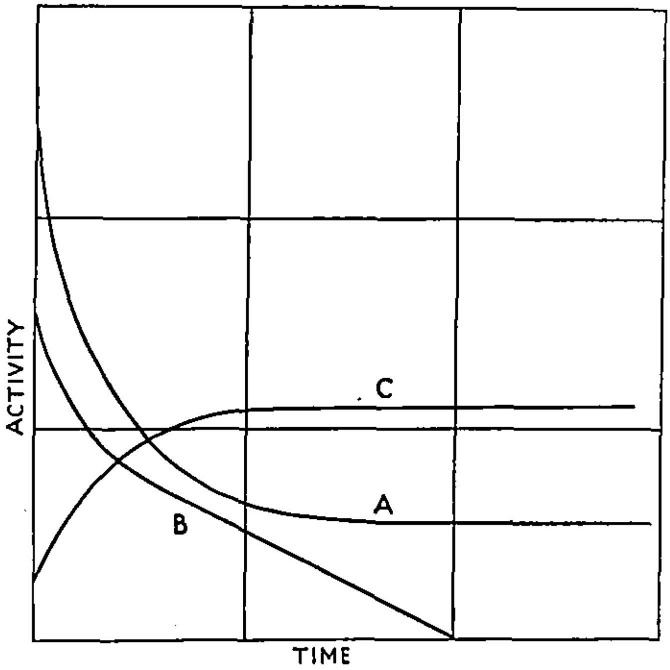


FIG. 6. Typical time-activity curves, showing three simple forms.

A, falls to steady value.
B, falls to zero.
C, rises to steady value.

It is with catalysts of the last type, where a steady fall occurs, that the question of regeneration becomes important;

it may be studied experimentally in the same way as the usual activity determinations. An example is illustrated in Fig. 7, where the change in activity of a vanadium oxide catalyst used for the conversion of cresol to toluene by hydrogenation at 440° under atmospheric pressure is plotted against time.[1] Owing to the gradual accumulation of tarry products on the surface of the catalyst, the activity fell as shown, but on treating the catalyst with a stream of air at the same temperature, the activity was restored practically to its initial value, and then fell off again in precisely the same way as before when more cresol was admitted.

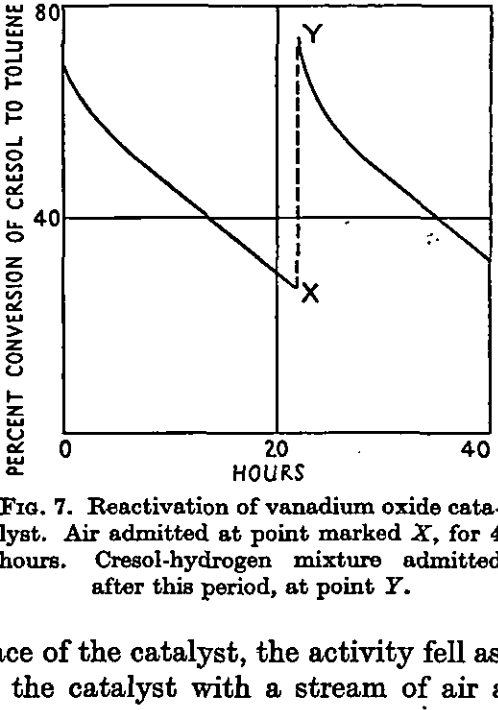


FIG. 7. Reactivation of vanadium oxide catalyst. Air admitted at point marked *X*, for 4 hours. Cresol-hydrogen mixture admitted after this period, at point *Y*.

Temperature.

In general, a rise in temperature will produce a greater catalytic activity, within the limits of the thermodynamic requirements of the reaction involved, but the highest useful temperature which can be used in practice will be restricted by several considerations. The most important of these will be the occurrence of secondary reactions, and of changes in

---

[1] Griffith, unpublished data.

the catalyst surface. In the synthesis of ammonia, for example, the percentage of NH_3 in equilibrium with H_2+3N_2 is higher the lower the temperature, while the velocity with which equilibrium is established increases greatly as the temperature rises. A choice has to be made therefore between extreme conditions which give a high degree of conversion with very small through-put, or a small conversion in a very short time. As regards secondary reactions, the case of conversion of cresol to toluene will again serve as an example; in Fig. 8 are shown the temperature-activity curves for vanadium oxide and chromium oxide catalysts, both being characterized by a rise to a maximum beyond which a steep fall occurs. This drop at about 450° is due to the rapid increase in polymerization reactions which lead to covering of the surface with pitch-like compounds. Similar effects were observed by Maxted[1] in the oxidation of aromatic hydrocarbons with vanadium catalysts, particularly tin vanadate. The effect of temperature on the yield of benzoic acid from ethyl benzene, or of phthalic anhydride from *o*-xylene is shown in

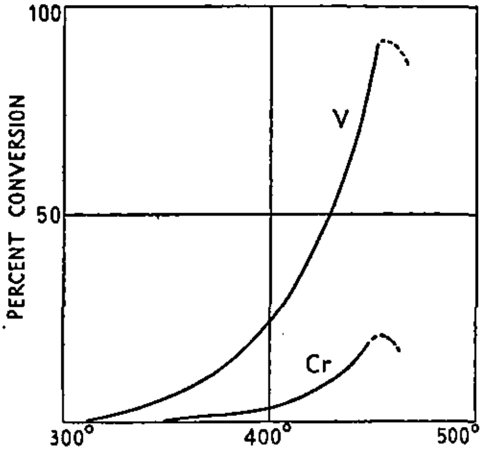


FIG. 8. Effect of temperature on conversion of cresol to toluene, with vanadium oxide and chromium oxide catalysts. Above 450° the loss of activity is so rapid that comparative results cannot be obtained.

---

[1] *J.S.C.I.*, 1928, 47, 101.

Fig. 9. The loss of activity at the higher temperatures in this case is due to further decomposition of the primary reaction products.

Under certain conditions there may be a maximum in the temperature-activity curve due to preferential adsorption of one of the reactants; this case is discussed more fully in Chapter VII as it is of considerable theoretical interest.

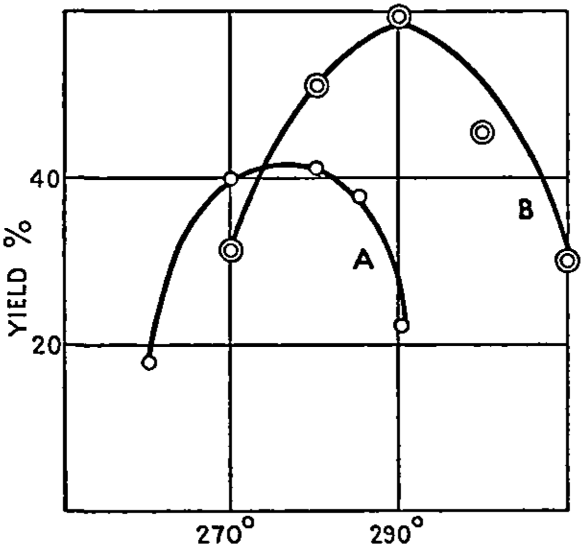


Fig. 9. Oxidation of hydrocarbons.
A, ethyl benzene.
B, *o*-xylene.

In the comparison of different catalysts it is generally preferable to keep the temperature constant, and it is only in cases where information regarding the energy of activation for a reaction is required that velocity measurements at different temperatures become important. The order of activity of different catalysts does not, however, necessarily remain the same at all temperatures.

CHAPTER II

ADSORPTION

THE study of the adsorption of gases by solids has played such an important part in the elucidation of the nature of catalytic action that an early account of the relation between the two will assist in the later development of the subject.

Direct determination of adsorption.

In Fig. 10 a typical apparatus for the determination of adsorption is shown. The catalyst is contained in a bulb *A* which may be heated to any desired temperature and which is connected to a water-jacketed burette *D*, a manometer and McLeod gauge *B*, and, by way of drying tubes which may include traps cooled in liquid air, an evacuation system *C*. The gas or vapour which is being studied is supplied from a suitable source through a purifying train *E*. The particular modifications of the apparatus which may be required will depend on the temperature and pressure of the system to be studied, and on whether it is desired to recover the desorbed gases or not; in the latter case a pump of the Sprengel or Töpler type will be necessary. The measurement of very low pressures may require a gauge of higher sensitivity than the McLeod type can give, and the latter is not suitable for determinations with condensible vapours.

Illustrations of other forms of apparatus will be found in a paper by Pease[1] and in McBain's book, *The Sorption of Gases by Solids* (Routledge, 1932). Before carrying out any measurements it is essential to ensure that the catalyst surface is properly cleaned, and this may involve evacuation at elevated temperatures for periods of several days. At the same time precautions must be taken to avoid overheating the catalyst, and to make certain that the material is being tested in the same form as that used in determinations of catalytic effect.

Calibrations for dead space and for temperature gradient must be made and are preferably done with an inert gas such as argon. The methods of use of the apparatus for measure-

---

[1] *J.A.C.S.*, 1923, 45, 1196.

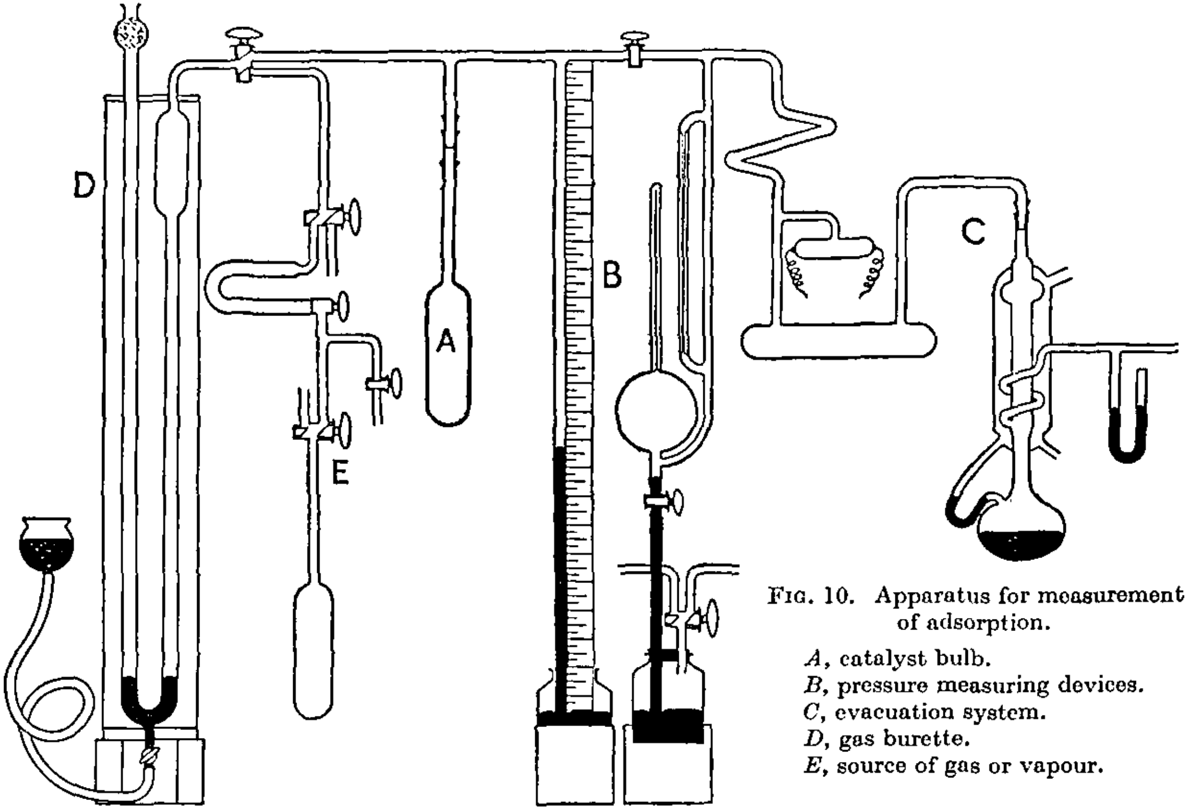


FIG. 10. Apparatus for measurement of adsorption.

A, catalyst bulb.
B, pressure measuring devices.
C, evacuation system.
D, gas burette.
E, source of gas or vapour.

ments at constant volume or constant pressure are sufficiently obvious to require no detailed description.

In the direct determination of adsorption velocity with condensible vapours at low total pressures, special precautions are necessary in order to obtain sufficiently accurate measurements. As there are difficulties associated with the use of gauges of the Pirani type for substances such as hydrocarbons of high molecular weight, the most satisfactory instruments appear to be either an aneroid manometer such as that described by Stewardson,[1] used as a null instrument in which the balancing pressure can be accurately measured, or a McLeod gauge surrounded by a constant-temperature jacket heated so that condensation of liquid cannot take place.

Weighing of the adsorbed substance.

The methods of McBain and Bakr[2] and McBain and Tanner[3] involved actual measurement of the change in weight during adsorption. The sorption balance consisted essentially of a silica spring constructed of threads about 0·02 cm. in diameter made into a coil about 1·25 cm. in diameter, with 15 turns giving a total length of about 6 cm. The sensitivity varied with the coil diameter, but was limited by the total load carried. Changes in the length of the spring could be measured to 0·002 cm., which gave a maximum useful accuracy of 2×10^{-4} gm. The whole spring could be sealed into an all-glass apparatus (Fig. 11)

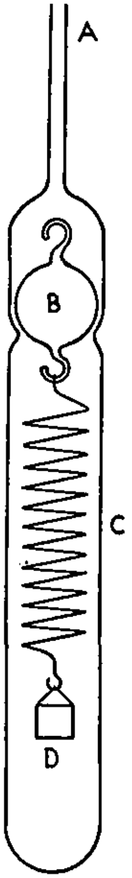


FIG. 11.
The Sorption Balance.
A, to vacuum and gas supply.
B, support for spring; hollow glass sphere.
C, silica spring.
D, bucket of fine platinum foil.

---

[1] *J. Scient. Instr.*, 1930, 7, 217.

[2] *J.A.C.S.*, 1926, 48, 690.

[3] *P.R.S.*, 1929, 125 A, 579.

and kept at any temperature and pressure during the experiment.

The microbalance was more sensitive, as with a load of 0·3 gm. it could be read to 4×10^{-9} gm., it consisted of a quartz beam carrying an iron pin and resting on carborundum points, which was brought back to a fixed position by alteration of the current in a magnetic field. In spite of the accuracy with which these determinations can be made, however, the method is unfortunately not applicable to the investigation of adsorption velocities, particularly at low total pressures, as the quantities involved are too small. It has, however, obvious advantages for the rapid measurement of total adsorption in the case of substances with high molecular weight.

Heat of adsorption.

Although it is frequently more convenient to calculate heats of adsorption from isotherms, the differential heat of adsorption for small increments of pressure is of considerable theoretical interest and may be determined directly by means of an adsorption calorimeter, such as that described by Beebe and H. S. Taylor,[1] or by McKie.[2] The most recent modification of this instrument is due to Garner and Kingman[3] and is shown in Fig. 12. A thermocouple A enters the vacuum

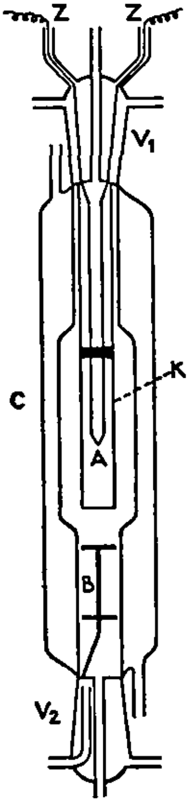


FIG. 12. Improved double-walled adsorption calorimeter.
A, thermocouple embedded in adsorbent.
B, silica disks to reduce radiation.
C, double-walled glass vessel.
K, gauze container for adsorbent.
V_1, V_2, water-cooled stoppers.
Z, connexions to millivoltmeter.

---

[1] *J.A.C.S.*, 1924, 46, 43.
[2] *J. C. S.*, 1928, 2871.
[3] *T. Farad. Soc.*, 1931, 27, 322.

calorimeter at ZZ and is connected to a Moll galvanometer of high sensitivity, which gives a deflection of 16 cm. per degree at a distance of 2 metres. The cold junction temperature must be kept constant to 0·003° and the switch between thermocouple and galvanometer is immersed in an oil bath. The catalyst is suspended in the double-walled vessel C by means of a platinum cage K, and the end stoppers V_1 and V_2 are water cooled. The whole instrument is kept in an air thermostat during a determination.

The chief shortcomings of the instrument are (1) the poor thermal conductivity of the catalyst material, (2) the very small amounts of gas which are in the system during the early stages of measurement, also leading to bad heat conduction, (3) compression of unadsorbed gas by further quantities admitted, and (4) the slowness with which equilibrium is sometimes established, with consequent masking of small heat effects. Errors may also be introduced by incomplete reduction of a metal oxide, for example, or on account of traces of gases remaining adsorbed on the surface. The first difficulty is largely overcome by the use of thin layers of catalyst and the second by admitting an inert buffer gas, such as helium, to the system; but allowance for the third is of doubtful value, and the fourth can only be dealt with approximately by extrapolation methods

Determination of the heat of adsorption of hydrogen on a bare tungsten wire has been carried out by Roberts,[1] by using the wire itself as a calorimeter and determining the change in its resistance. The method can only be applied successfully when adsorption is practically complete at very low pressures, and refers primarily to cases of true chemisorption. As an example of the results obtained, the figures in Table 2 may be considered for an experiment where hydrogen was admitted in four stages.

The number of unfilled spaces was calculated from the saturation value finally reached. There is clearly a decrease in the heat of adsorption as the surface is covered, which is attributed to changes in the contact potential under the influence of atoms already held, so that the initial maximum

---

[1] *P.R.S.*, 1935, **152 A**, 445.

heat of adsorption can only be determined by extrapolation as indicated in Fig. 13. No attempts have yet been made to apply this method to cases of activated adsorption (see p. 27), and it seems doubtful whether this could be done without introducing correction factors so large as to make the results very unreliable.

TABLE 2

Adsorption of hydrogen on tungsten wire

Admission	H_2 *molecules adsorbed*	*Unfilled spaces on surface, mean*	*Heat of adsorption K-cals/mol.* H_2
1	$1{\cdot}19\times10^{14}$	$7{\cdot}18\times10^{14}$	34·2
2	1·18 ,,	4·8 ,,	28·5
3	1·17 ,,	2·46 ,,	20·3
4	0·64 ,,	0·64 ,,	17·5

Adsorption and catalyst activity.

The idea that catalytic activity was related to the adsorptive power of a surface for one or more of the reactants has obvious attractions in offering an explanation of increased velocity as due to a high local concentration and a greater probability of collision. Qualitative investigation of this point quickly showed that adsorption on catalysts did occur; Hoover and Rideal, for example,[1] demonstrated that hydrogen, ethylene, and alcohol were rapidly adsorbed by alumina catalysts which led to the dehydrogenation of alcohol.

A more exhaustive study by Fryling[2] in the case of nickel catalysts promoted by thoria or by cerium oxide involved measurement of the heat of adsorption of hydrogen at 0°, and it was found that a qualitative relation existed between the activity of the catalyst and the heat of adsorption. Lazier and Adkins[3] also described a qualitative agreement between the adsorptive capacity and the activity of a catalyst used for ethylene hydrogenation. A similar agreement was found by Garner and Kingman[4] for the case of the adsorption of carbon monoxide and hydrogen on zinc oxide—chromium oxide catalysts for methanol, which agreed with

[1] *J.A.C.S.*, 1927, 49, 116.

[2] *J. Phys. Chem.*, 1926, 30, 818.

[3] *J.A.C.S.*, 1924, 46, 2291.

[4] *T. Farad. Soc.*, 1931, 27, 322.

the earlier observations of H. S. Taylor and Kistiakowsky[1] that mixed catalysts containing the two oxides had a much greater adsorptive capacity for hydrogen than was shown by zinc oxide alone. H. S. Taylor and Dew[2] also found that the most active ammonia catalysts showed the highest values for the heat of adsorption of hydrogen.

At the same time, other observers failed to detect any such relation. Hoskins and Bray,[3] for example, measured the adsorptive capacities of manganese dioxide, copper oxide, and mixtures of the two for carbon monoxide and dioxide and for oxygen, but the results showed no similarity to the activity of the catalysts for the combustion of carbon monoxide.

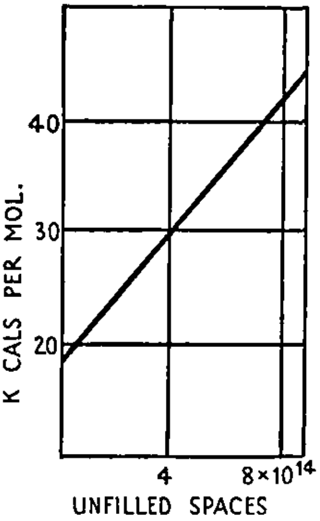


FIG. 13. Change in heat of adsorption of hydrogen on clean tungsten wire. The initial value of 45 K-cals is obtained by extrapolation to $8{\cdot}8 \times 10^{14}$ unfilled spaces, which is the total available. The line given is the mean of five series of determinations.

Some experimental data of Frankenburger[4] suggested that forces rather different from those of normal adsorption might come into play during catalysis. He experimented with deposits formed by evaporation of metallic iron on to a cold wall, and found that each atom of iron took up one atom of hydrogen or of nitrogen, but that as the size of the metal crystals grew from 10 to 150 Å the ratio of Fe : H_2 increased from 1 : 1 to 9 : 1, and the most active iron catalyst such as was used for ammonia synthesis, had a ratio of about 70 : 1. Nikitin[5] at an earlier date had made the very interesting observation that pyrophoric iron, which gave practically no adsorption of hydrogen at —80° and at 16°, took up large amounts at —185° and at 380°, that adsorbed at the high temperature not being given up on evacuation at room temperatures.

---

[1] *J A C S.*, 1927, **49**, 2468.

[2] *J. Phys Chem*, 1927, **31**, 277.

[3] *J.A.C.S.*, 1926, **48**, 1454.

[4] *Z. Elektrochem.*, 1929, **35**, 920.

[5] *Z anorg. Chem.*, 1926, **154**, 130.

No real advance in this treatment of the subject was made until the experiments of Benton and White[1] and of H. S. Taylor,[2] in which the adsorption measurements were carried out over a much wider temperature range. The fact that adsorption was now measured at temperatures approximating to those involved in the reactions themselves was the real key to progress that has been made. Benton and White studied the adsorption of hydrogen on nickel and obtained isobars, shown in Fig. 14, which were of an unexpected and novel type, and which could only be explained by assuming two kinds of adsorption to be taking place at different temperatures. In the upward-sloping parts of the curves both kinds are occurring, and the position of this transition is slightly affected by the pressure of the system, as its effect is unequal for the two types. The flat portion of the curve at 600 mm. pressure is also of great interest as it indicates saturation of the surface by hydrogen over a relatively wide temperature range.

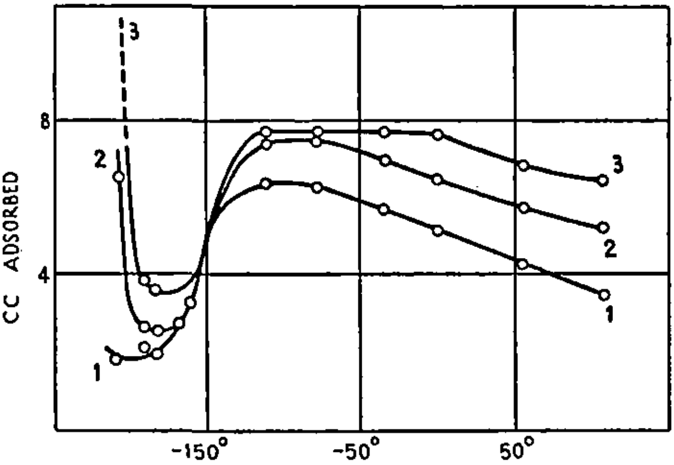


FIG. 14. Adsorption of hydrogen by nickel.
1, at 2·5 cm. pressure.
2, at 20 „ „
3, at 60 „ „

---

[1] *J.A.C.S.*, 1930, 52, 2325.
[2] Ibid., 1931, 53, 578.

Activated adsorption.

The general case of this dual type of adsorption was presented by H. S. Taylor,[1] that which takes place at the higher temperature and with a measurable velocity being defined as 'activated adsorption'. The ideal curves to be expected from the two kinds of adsorption are shown in Fig. 15, where the actual curve observed in experiments is also indicated; this latter is recorded only on account of failure to reach true equilibrium, in the period used, at the lower temperatures.

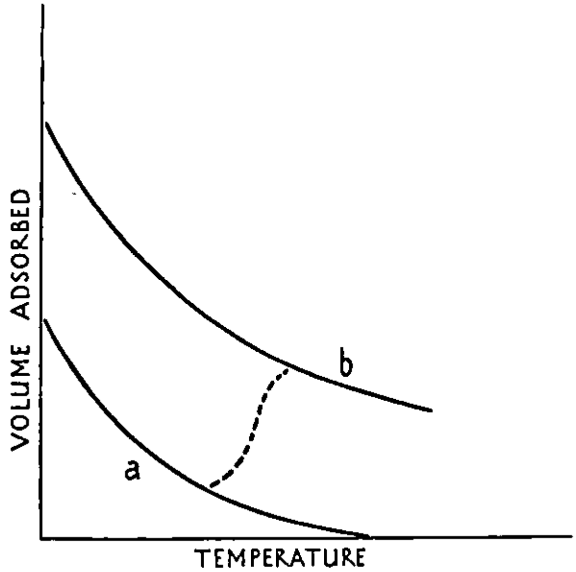


FIG. 15. Typical isobars for normal (*a*) and activated (*b*) adsorption. The experimental curve follows *a* until the point where it is joined by the broken line, by which transition to *b* is made.

For the low-temperature curve a high velocity and a low heat of adsorption is to be expected, but the slow adsorption with a relatively small velocity resembles a reaction at a surface and has a high heat of adsorption and a characteristic energy of activation. Since changes on curve *b* involve a large activation energy, the part at lower temperatures will only be realized in practice by heating the system to a higher temperature and then allowing it to cool; even under these

---

[1] Loc. cit.

conditions the final attainment of equilibrium will often be so slow that the determined curve will lie below *b* but well above *a*.

The characteristics of this process are shown in Fig. 16, where typical velocity curves are presented for the adsorption of hydrogen on a molybdenum oxide catalyst containing silica as a promoter.[1] Similar curves are obtained with a wide variety of other gases in contact with other surfaces.

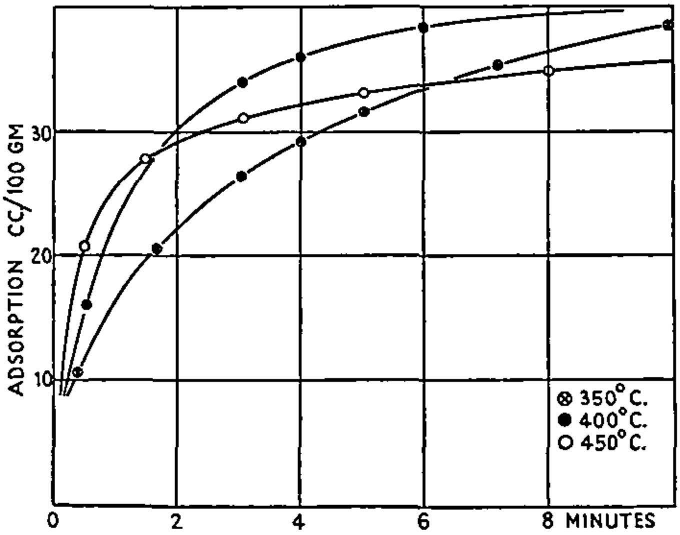


FIG. 16. Velocity of adsorption of hydrogen on molybdenum oxide-silica catalyst at different temperatures.

It is from these curves that the heat of adsorption, for the activated stage, can be calculated by determining the equilibrium value at different temperatures, using the relation

$$\log \frac{V_1}{V_2} = \frac{\lambda}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right),$$

where V_1 and V_2 are the volumes adsorbed at the two temperatures T_1 and T_2 on the absolute scale, and λ is the heat of adsorption. No direct measurements, by the use of a calorimeter, have yet been made.

---

[1] Griffith and Hill, *P.R.S.*, 1935, 148A, 194.

The apparent energy of activation E is also derived from the curves, using the time of half-saturation as inversely proportional to the adsorption velocity and selecting a suitable temperature interval for application of the equation

$$\log \frac{K_2}{K_1} = \frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right),$$

where K_1 and K_2 are the velocities at the two temperatures.

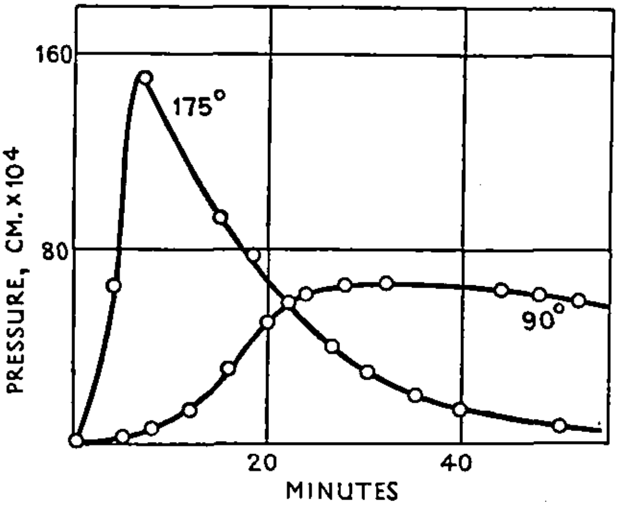


FIG. 17. Adsorption of hydrogen on zinc oxide-chromium oxide catalyst. Change in pressure on raising temperature.

The energy relations existing on the catalyst surface are more fully discussed in Chapter VII.

During an actual determination of adsorption the effect of raising the temperature may often be first to increase the pressure in the system owing to the displacement of the gas held by van der Waals adsorption, followed by a decrease in pressure as the new type of adsorption comes into play. The relative importance of these opposing effects will depend on temperature, as typical curves obtained by Garner[1] show for the case of hydrogen in contact with zinc oxide—chromium oxide mixtures (Fig. 17). At 175° there is a rapid displacement of gas, but the pressure then falls again almost as

---

[1] *T. Farad. Soc.*, 1932, 28, 261.

rapidly, while at 90° the velocity of activated adsorption is very small and only a very slight downward drift in the pressure-time curve can be observed.

The case of adsorption of hydrogen on manganese[1] is another example of this activated adsorption, having a van der Waals heat of adsorption of 1,900 cals. per mol and a value of 19,000 for the activated adsorption. When the study was extended to promoted manganese catalysts containing chromium oxide, the results were still more striking.[2] Measurements were made with hydrogen on catalysts, which had been previously reduced with hydrogen, at temperatures up to 444°, and by velocity measurements at different temperatures the energy of activation could be calculated. In Table 3 data for a promoted catalyst are given, which may be compared with an initial energy of activation of 12,000 rising to 20,000 cals. for the unpromoted manganese oxide.

TABLE 3

Adsorption of hydrogen on promoted manganese oxide catalyst

Amount adsorbed	*Time*		*E, cal./mol*
	At 132°	*At* 100°	
First 10 c.c.	3·2 mins.	6·0 mins.	5,920
10–15 „	7·3 „	20·0 „	9,500
15–20 „	15·9 „	48·0 „	10,400
20–25 „	37·2 „	111·5 „	10,400

These figures not only show that the first portions of hydrogen adsorbed, i.e. those taken up by the most active parts of the surface, require a lower activation energy than the final portions, but that the activation energy in the case of the unpromoted catalyst is uniformly much higher than when a promoter is present. The total volume adsorbed is also greater with the promoted catalyst.

There is thus some kind of relation between the quantity of hydrogen taken up in activated adsorption, the energy of activation of this type of adsorption, and the activity of the

---

[1] H. S. Taylor and Williamson, *J.A.C.S.*, 1931, 53, 813.

[2] Ibid., 1931, 53, 2168.

catalyst. Further cases of activated adsorption will be also discussed as they assist in discussion of promoter action.

The adsorption of hydrogen on zinc oxide, zinc chromite, and zinc molybdate was measured by H. S. Taylor and Strother,[1] and it was found that zinc oxide alone exhibited three different types of adsorption as shown in Fig. 18. The first of these is the van der Waals, but the second and third are both activated, having increased velocities as the temperature rises, and are characterized by different energies of activation.

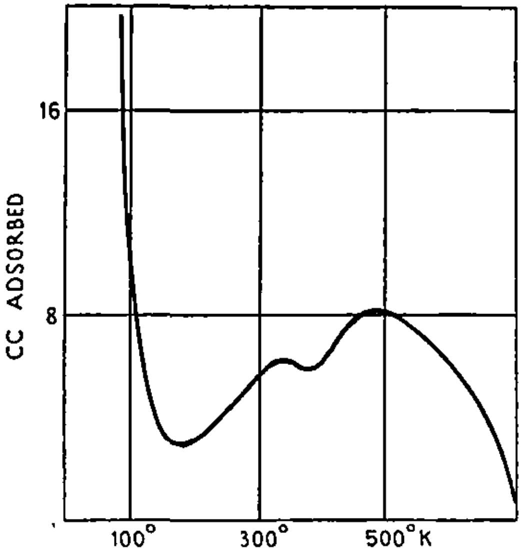


FIG. 18. Isobar at 760 mm. for adsorption of hydrogen on zinc oxide.

Benton[2] also detected three-stage adsorption of hydrogen and carbon monoxide on copper and iron, of nitrogen on iron, and of hydrogen on nickel, and showed how the three stages could be isolated by study over a sufficiently wide temperature range, particularly by observing the effect of rapid temperature changes. They concluded that the third stage consisted of solution, and that this was necessarily preceded by activated adsorption.

---

[1] *J.A.C S.*, 1934, 56, 586

[2] Ibid., 1932, 54, 1820, *T. Farad. Soc.*, 1932, 28, 202.

The experiments of Morozov[1] were concerned with a more detailed investigation of the behaviour of hydrogen on iron catalysts prepared by prolonged reduction of the precipitated oxide. It was shown that the velocity of activated adsorption increased rapidly as the temperature rose so that at about 200° it was practically instantaneous, and changes in pressure recorded after 1 minute could be considered as due to a distinct process. The three possible processes for hydrogen on iron are shown separately in Fig. 19. The activation energy for curve *B* is about 20,300 cals./mol, but for *C* is only about 8,500 cals., and the latter is again considered to be a solution process.

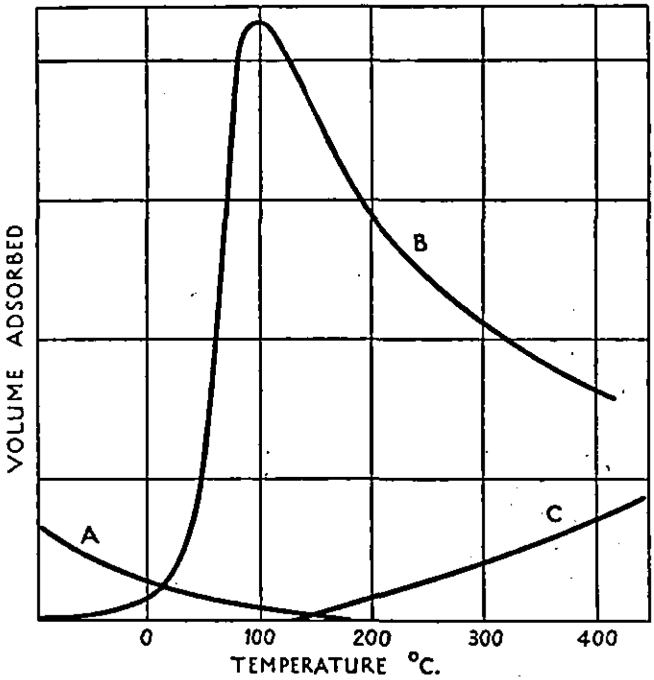


FIG. 19. Adsorption of hydrogen on iron.
A, van der Waals.
B, activated.
C, diffusion.

Separation of three-stage process; at 150–200° the activated adsorption becomes so rapid that the diffusion can readily be identified by its much slower rate.

---

[1] *T. Farad. Soc.*, 1935, 31, 659.

Emmett and Harkness[1] have also investigated the case of hydrogen adsorption on iron catalysts, but at lower temperatures than those reached by Morozov. Their 760 mm. isobar is shown from —200° to 450° in Fig. 20, where van der Waals adsorption can be observed up to about —100°. At —78° activated adsorption is relatively fast, and above 100° a second type of activated adsorption comes into action; these two were differentiated by their effects on the conversion of ortho- to para-hydrogen and on the van der Waals adsorption, the higher temperature type decreasing the extent of both (see p. 51). Unfortunately, owing to the overlap of the individual processes, comparative figures for the energy of activation for the two stages could not be obtained, and the nature of the difference between them cannot yet be explained.

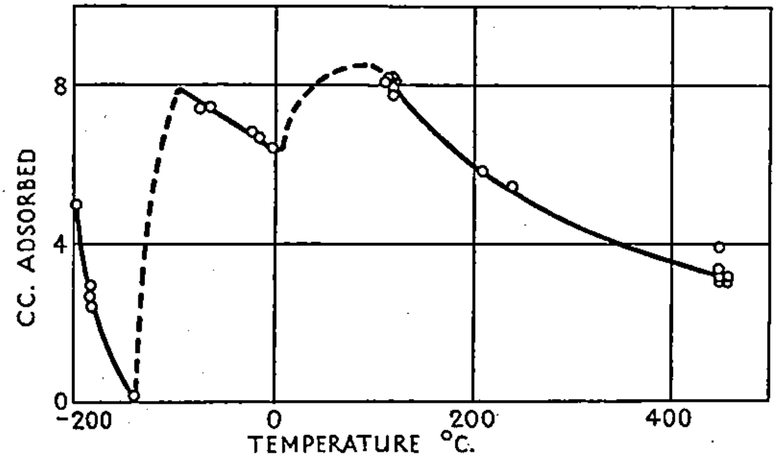


Fig. 20. Adsorption isobar for hydrogen on promoted iron catalyst.

The evidence available suggests that the second type of activated adsorption is a distinct process not related to catalytic action. If the catalyst contained two components which came into play at different temperatures, it might be possible for separate activated adsorption to occur on each, but such effects have not yet been observed with mixed catalysts, and the idea is in conflict with Taylor's data concerning mixtures

---

[1] *J.A.C.S.*, 1935, **57**, 1631.

of zinc oxide and chromium oxide, in which only one stage of activated adsorption could be detected and the solution effect was entirely absent.

Activated diffusion.

The most instructive experiments which have been carried out, in order to investigate the nature of activated diffusion more closely, have considered the comparative behaviour of hydrogen and deuterium. Melville and Rideal[1] have studied the reduction of copper oxide with the two isotopes, and found that photochemically produced atoms of H or D gave identical rates, but that the thermal reduction with H_2 always took place more rapidly than that with D_2 as shown in the

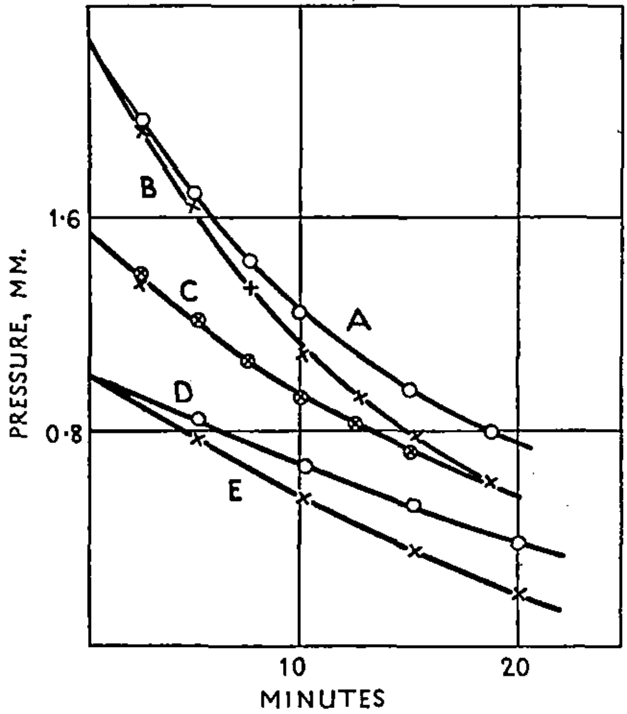


Fig. 21. Reduction of copper oxide.
A, 47 per cent. D_2 at 201°.
B, H_2 at 201°.
C, atomic H or D.
D, 47 per cent. D_2 at 156°.
E, H_2 at 156°.

---

[1] *P.R.S.*, 1935, 153 A, 77.

curves of Fig. 21. No inhibition due to water formation could be detected, so that the phenomenon could not be attributed to the slower evaporation of D_2O from the surface. The difference was therefore due to the respective rates of diffusion of H_2 and D_2 or the corresponding hydride and deuteride, or to a difference in the energy of activation of the hydride and deuteride after they had diffused through a layer of previously formed metal to reach an oxide molecule.

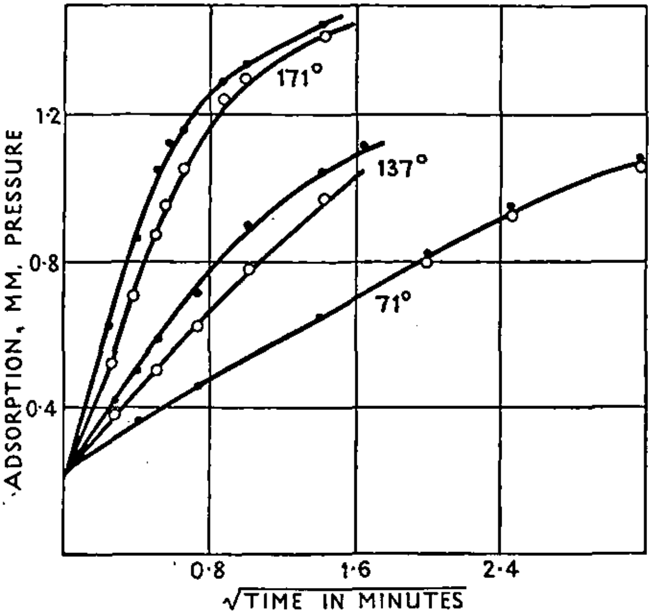


FIG. 22. Adsorption of hydrogen and deuterium on copper. Initial pressure 7·0 mm. The lower curve at each temperature refers to 70 per cent. D_2; at 71° the rates are identical.

The sorption of hydrogen and deuterium by metallic copper was accordingly investigated to attempt to decide which of the above alternatives was more probable. It was found that the results were identical for the two isotopes at lower temperatures, but slightly more rapid for H_2 in its later stages at temperatures above about 100°, as shown in Fig. 22. The initial rapid adsorption was equal for hydrogen and deuterium, and the rates of desorption were also identical at the lower temperatures; these results are similar to those recorded by Pace and H. S. Taylor[1] for adsorption on nickel and on chromium oxide.

It was concluded that the slow process, which had a characteristic energy of activation, was a complex reaction involving migration and diffusion of atoms or of hydride and deuteride. For this step the ratio of the velocities with the two isotopes was found to be only slightly less than that to be anticipated from the difference in the zero-point energy of CuH and CuD. Further reference to this point is made in Chapter VII.

In a more detailed study of the diffusion of hydrogen and deuterium through a copper film Melville and Rideal[2] found that the rate-determining step was not one taking place at the gas-metal interface, but involved the penetration of hydrogen into the metal through the monomolecular layer of chemi-sorbed hydrogen atoms which Roberts experiments have shown to exist (see p. 23). Hydrogen always diffused more quickly than deuterium on account of its greater solubility and greater mobility in the metal.

The significance of these facts in connexion with catalytic changes occurring at a surface is probably much greater with regard to determining the character of the surface itself than with respect to any influence on the catalysed reaction, once the surface has been formed. It is clear that activated diffusion or migration cannot alone account for the observed effects in such cases as that of a single molecule decomposing in contact with a catalyst, and it is difficult to visualize diffusion as being possible with a large molecule such as dekalin. Nor is it likely that activated diffusion has any bearing on reaction velocity in cases where the change occurs by collision of a gas molecule with an adsorbed molecule.

Similar conclusions may be drawn from the work of Barrer[3] on the diffusion of gases through silica glass at temperatures up to 1,000°. It was found that the same type of exponential temperature coefficient of diffusion velocity applied for helium, hydrogen, oxygen, nitrogen, neon, and argon, and

---

[1] *J. Chem. Phys.*, 1934, **2**, 578.

[2] *P.R.S.*, 1935, **153** A, 89.

[3] *J.C.S.*, 1934, 378.

that energies of activation varied from 5,780 cals. per gm.-mol. for helium to 48,000 cals. for argon. The process took place either by passage through the silica lattice, as was the case with hydrogen, helium, and neon at the higher temperatures, or through slip planes in the case of the heavier gases and also the light gases at lower temperatures. The migration occurred with molecules from the adsorbed layer and not directly from the gas phase, and the energy of activation for the process arose from dynamic polarization resulting in van der Waals cohesion, and also from exchange forces resulting in gas-solid repulsion.

The permeability of the silica decreased considerably on prolonged heating, except with hydrogen and helium, on account of surface crystallization leading to a decrease in the width of slip planes. The effect of introducing alkali atoms into the surface in the form of silicate glasses was also to reduce the space available for lattice migration. The fact that the energy of activation for the diffusion of hydrogen was the same over a wide range of different samples of silica indicates that the specific effects usually associated with catalysis were absent, and the observation that the largest energy of activation was shown by argon leads to the conclusion that the effects are physical and not chemical.

The existence of an activated stage in the sorption of a gas by a solid does not therefore necessarily involve catalytic activation of the molecule.

Observations by Jijima[1] indicate that a third stage of adsorption of hydrogen may also occur on nickel, which is attributed to diffusion.

Activated adsorption and catalyst activity.

Although Taylor has found enhanced adsorption effects with two component catalysts, he has also shown that these do not necessarily occur.[2] Zinc oxide-molybdenum oxide mixtures, on the contrary, gave lower adsorption of hydrogen and a higher energy of activation than zinc oxide alone.

[1] *Sci. Papers Inst. Phys. Chem.*, Tokyo, 1935, **26**, 45.

[2] *T. Farad. Soc.*, 1934, **30**, 1178.

Not only hydrogen can be adsorbed in this way, in fact there is reason to suppose that almost any compound or element which is taking part in contact catalysis must be involved in activated adsorption, and direct evidence for this assumption is rapidly accumulating. Emmett and Brunauer[1] measured the adsorption of nitrogen on iron catalysis at temperatures between 200° and 450°, and found that the energy of activation was lowest in the case of catalysts promoted by alumina and potassium oxide, while the velocity of adsorption was lowest with pure iron.

H. S. Taylor and Turkevitch[2] determined the behaviour of ethylene, methane, ethane, and propane on manganese chromite and on copper catalysts at temperatures up to 444° and found that activated adsorption of all the hydrocarbons took place, although the results were somewhat complicated by decomposition. In view of the variety of the surfaces which are active and of the products obtained, it was concluded that the adsorption could take place by union of either carbon or hydrogen atoms in the molecule with the active centre of the catalyst, and this suggestion of the existence of surface complexes is strongly supported by the evidence of Farkas[3] and of H. S. Taylor (see below) who showed that the reaction $C_2H_4+D_2 = C_2H_3D+HD$ can take place in contact with catalysts.

TABLE 4

Adsorption of hydrogen on oxide catalysts

Catalyst	*Van der Waals adsorption c.c./gm. at 194·5° K.*	*Activation energy for 0·2 c.c.* H_2*/gm. at 405°*
ZnO	0·2	11 K. cals.
Cr_2O_3	0·7	19 ,,
$ZnO–Cr_2O_3$	0·6	1 ,,
MnO	< 0·1	20 ,,
$MnO–Cr_2O_3$	0·5	6 ,,

An interesting comparison between the normal van der Waals adsorption and activated adsorption is given by H. S. Taylor and Howard[4] for the case of hydrogen on chromium

---

[1] *J.A.C.S.*, 1934, 56, 35

[2] Ibid., 1934, 56, 2254

[3] *Chem. and Ind.*, 1934, 53, 489.

[4] *J.A.C.S.*, 1934, 56, 2259.

oxide gel which had been reduced at 375°, with precautions to avoid overheating of the surface, and a number of other catalysts as shown in Table 4. It is evident that the mixed catalysts do not necessarily show increased surface as judged by van der Waals adsorption, but that there is a considerable decrease in the energy of activation for the activated stage.

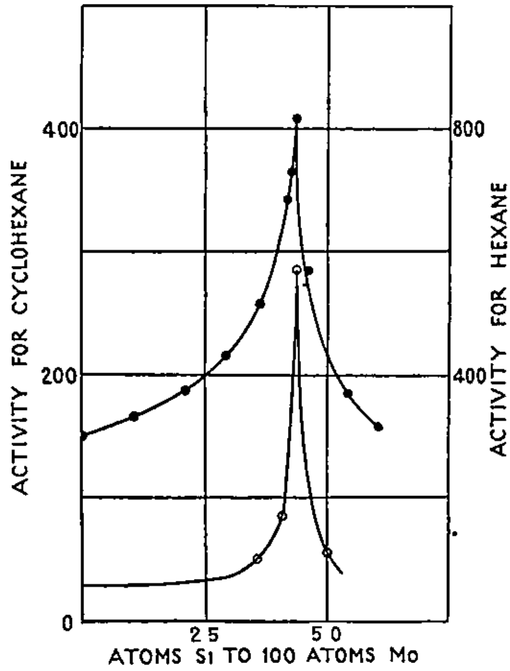


Fig. 23 Effect of promoter concentration on the activity of molybdenum oxide catalysts for decomposition of hydrocarbons at 500°.

The relationship between activated adsorption and catalyst activity has been examined by Griffith and Hill[1] in the case of hexane and cyclohexane with molybdenum catalysts promoted by silica. The activity for the decomposition of the hydrocarbon was related to promoter concentration in the manner shown in Fig 23, and the change in the quantity of a hydrocarbon adsorbed with increasing promoter concentra-

---

[1] *P.R S.*, 1935, 148 A, 194.

tion is given in Fig. 24. The close similarity in form of the two sets of figures and the exact agreement of the maxima, including the case of benzene which does not undergo any decomposition, make a convincing argument as to the reality of the effect.

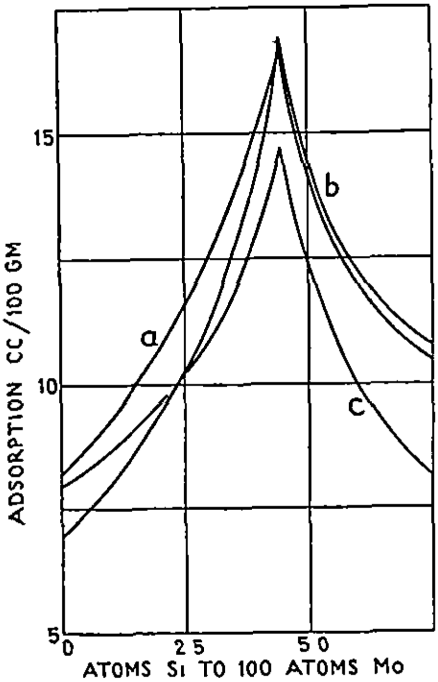


FIG 24 Effect of promoter concentration on the adsorption of hydrocarbons by molybdenum oxide catalysts at high temperatures

The nature of activated adsorption.

The fact that activated adsorption must not be considered synonymous with chemi-sorption has been stressed by Roberts.[1] By using the accommodation coefficient of Knudsen[2] for neon as an indicator for the condition of a tungsten surface, Roberts has carried out some illuminating measurements with hydrogen and oxygen in contact with the perfectly clean metal. The change in the accommodation coefficient for neon when hydrogen was admitted to the system showed that the surface was saturated with the latter at very low pressures, and that the total amount of hydrogen taken up corresponded very closely to the presence of one hydrogen atom attached to each surface tungsten atom, when the latter was calculated from the known dimensions of a wire, and the lattice constants for the crystal.

Saturation of the surface with hydrogen took place extremely rapidly even at 79° K., and had none of the characteristics of activated adsorption which has been shown to occur with hydrogen on tungsten catalysts.[3] Similar results

---

[1] *P R S.*, 1935, **152** A, 445, 464, 477.

[2] *Ann. Physik*, 1911, **34**, 593.

[3] Frankenburger and Hodler, *T. Farad. Soc.*, 1932, **28**, 229.

were obtained when oxygen was adsorbed on a bare tungsten wire, but a second molecular film could also be formed on empty spaces remaining in the atomic film, or formed by diffusion of oxygen from the surface into the body of the metal.

The most interesting results, however, were obtained when hydrogen was admitted to the tungsten surface which was already covered with oxygen, as under these conditions a relatively slow process could be identified which was very similar to activated adsorption. In the alternative process of admitting oxygen to the wire which was covered with hydrogen, the latter was simply displaced very rapidly from the surface, but no formation of water took place.

Although this series of investigations is not yet completed, it does appear likely that activated adsorption of hydrogen only occurs on a surface which contains adsorbed oxygen (or other foreign molecules) or in which oxygen is an integral part of the surface. The conditions under which the activated adsorption of substances other than hydrogen can take place would obviously be worthy of further experiment along these lines; the results obtained by Frankenburger and Messner[1] for the adsorption of nitrogen on tungsten, for example, appear to be capable of alternative interpretations which approach closely to chemi-sorption. In the decomposition of ammonia on tungsten catalysts also, the formation of an imide or nitride should be distinguished from activated adsorption.

Criticism of the theory of activated adsorption was chiefly based on the assumption that all the effects could be explained on the basis of solution,[2] or as being due to the presence of impurities on the surface,[3] but there are convincing arguments against both these views. The effects observed are often of a much higher order than those which are known to be due to solubility. Further, the greatly increased quantities of gas which are taken up by promoted catalysts often containing extremely small amounts of the promoter, would

---

[1] *Z. phys. Chem.*, Bodenstein Festband, 593.

[2] Steacie, *J. Phys. Chem.*, 1931, **35**, 2112.

[3] Burrage, *T. Farad. Soc.*, 1933, **29**, 677.

not be expected in view of the influence of impurities on solubility. It is also highly improbable that hydrocarbon molecules could dissolve in metals or in their oxides at such high temperatures, particularly in the case of large molecules like hexane or propane. An even more convincing argument is brought forward by Smithells and Ransley,[1] who have found a relation between the activated adsorption of hydrogen on copper, iron, nickel, and molybdenum and its diffusion through these metals. Similar effects were detected in the case of nitrogen and molybdenum, but not with argon and helium; that the two latter gases will not diffuse through any metal was shown by Sieverts.[2] Finally, the evidence of Howard has disposed of the suggestion that impurities on the catalyst surface can account for the phenomena.[3] Chromium oxide catalyst was saturated with hydrogen at an elevated temperature, then cooled and evacuated at room temperature; the normal van der Waals adsorption of hydrogen at —78·5° was then measured. In Table 5 are given a series of results showing the extent of each type of adsorption, the activated gas which was retained being determined by difference between that pumped off and that originally taken up.

TABLE 5

Hydrogen adsorbed on chromium oxide at —78·5°

Activated H_2	0	0	75	0	48	5	22·7	0
Van der Waals H_2	26·3	26·7	13·5	26·9	15·9	24·5	19·6	26·7
Total	26·3	26·7	88·5	26·9	63·9	29·5	42·3	26·7

The several values for the clean surface having no activated hydrogen indicate the reproducibility of the measurements; the variation in the initial activated adsorption was attained by alteration in the original temperature of saturation.

The van der Waals adsorption is therefore considerably reduced by the presence of hydrogen held by activated adsorption; if diffusion effects were responsible for the observations, as suggested by Ward,[4] the contrary would be the case.

---

[1] *P.R.S.*, 1935, 150 A, 172.

[2] *Ber.*, 1912, 45, 2576.

[3] *T. Farad. Soc.*, 1934, 30, 278.

[4] Ibid., 1932, 28, 399, 426.

The fact that the van der Waals adsorption of nitrogen on the catalyst, which already held activated hydrogen, was of precisely the same nature and equally reproducible, makes the suggestion of the presence of impurities being responsible no longer tenable. These results also appear to dispose of Hinshelwood's suggestion[1] that the temperature effects might be partly due to changes in the solid state affecting, for instance, accessibility of Smekal cracks.

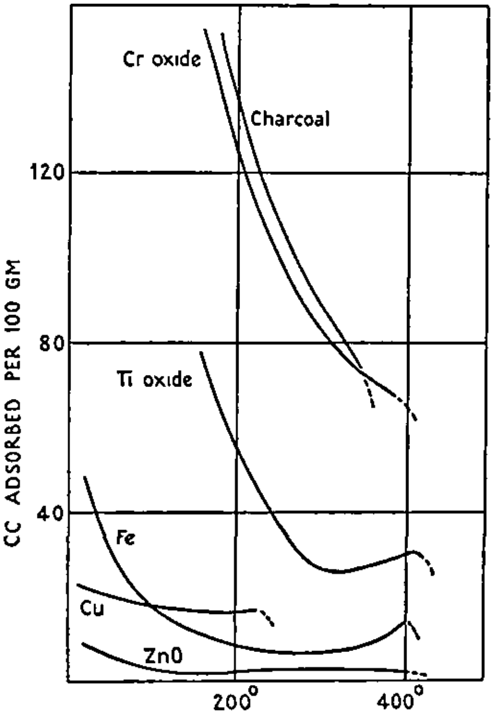


FIG 25. Adsorption of hexane by catalysts broken line indicates decomposition of hydrocarbon, which masks the activated adsorption in some cases

Although a relationship has been established between the activated adsorption of a single reactant and its velocity of decomposition on a particular series of catalysts, the position is not always so straightforward as this. A survey

---

[1] *T. Farad. Soc.*, 1932, 28, 415

of the behaviour of hexane on a wide range of oxides and metals has been made by Griffith and Hollings,[1] with the result that the surfaces investigated could be divided into two main classes. These are illustrated in the isobars of

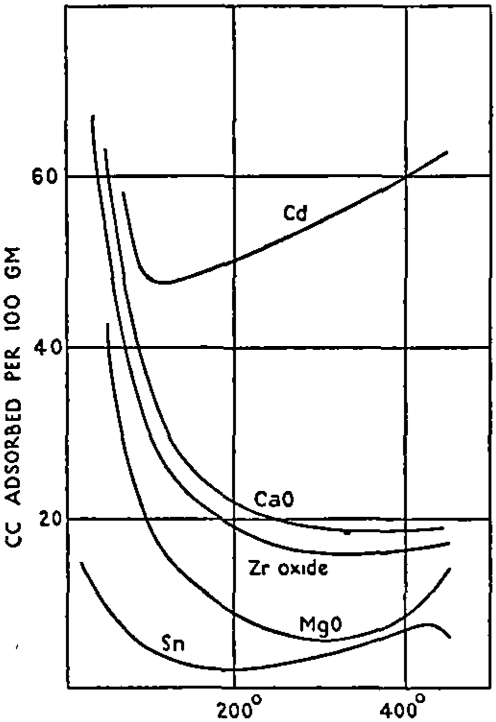


Fig. 26. Adsorption of hexane by catalysts which give no decomposition. The existence of activated adsorption is indicated.

Fig. 25 and Fig 26. The surfaces of the first type gave rise to decomposition of the hexane indicated by broken lines in the curve, at such temperatures that the existence of activated adsorption could not be definitely established, while those of the second type showed all the characteristics of activated adsorption without any sign of decomposition at 450°. On carrying out experiments by a dynamic method to compare the catalytic activity of the same substances, it was again found that practically no reaction was produced by

---

[1] Cf. *Nature*, 1934, **129**, 834.

those of the second type, although the adsorption with the latter was frequently the more extensive. This can be seen, for example, by comparing the curve for cadmium with that for copper or for titanium oxide; the latter was found to give vigorous decomposition, as indicated in Table 6 It is therefore evident that qualitative agreement can be found between

TABLE 6

Relative activity of catalysts for hexane decomposition

Catalyst	*Relative activity*
Cr oxide	360
C	1,350
Ti oxide	1,095
Fe	120
Cu	900
Zn oxide	180
Cd	0
Ca oxide	0
Zr oxide	50
Mg oxide	0
Sn	0

activated adsorption and catalytic effect but that the amount adsorbed is not the only factor involved. Several examples can be seen where the adsorption takes place to a large extent but little or no decomposition results, so that although catalytic activity is always associated with adsorption, the converse statement is not true. Questions of adsorption velocity and of the activation energy involved must be the determining factors in all such cases, as well as the actual position of the molecule on the surface (see p. 146). Unfortunately no information on these points is yet available for a series of catalysts similar to those described above, but the need for closer examination along these lines is obvious.

Adsorption of two reactants.

When two types of molecule are involved in a reaction the position becomes even more complicated, and simultaneous measurement of the adsorption of both cannot be made. By examining each separately it is possible to determine which is adsorbed more slowly, and which accordingly determines the reaction velocity. H. S. Taylor and Howard[1] showed in this way that the velocity of ethylene hydrogenation was controlled by the rate at which the hydrocarbon was adsorbed, as hydrogen was much more rapidly taken up.

Insley[2] has investigated the case of ethylene hydrogenation more closely with catalysts consisting of iron, cobalt, and nickel, and found that, although the isotherms were always higher in the case of metals reduced from their oxides than with those prepared from amalgams, the reaction velocities were generally of the same order. This again emphasizes the fact that adsorption velocity, rather than its total quantity, must play a vital part in determining the activity of a catalyst.

Even when full information of this kind is available, however, complications may arise owing to retardation by one of the reactants or one of the reaction products. If it is caused by a reactant it will probably be detected by the fact that excessive adsorption is found, or that saturation of the surface occurs over a wide temperature range and is revealed by a flat portion of the isobar. Harker[3] has found retardation due to the excessive adsorption of ethylene and of ethane when using copper catalysts deposited on diatomaceous earth for the hydrogenation of the hydrocarbon.

As another illustration of inhibition by reaction products the case of hydrogenation of tar oils at high pressures, investigated by Hollings, Griffith, and Bruce,[4] may be quoted. Molybdenum oxide catalysts were promoted by the addition of silica, which produced changes in activity shown in Fig. 27. The occurrence of two maxima suggested that these points would coincide with the optimum conditions of adsorption of hydrogen and hydrocarbons respectively. The results given for hydrogen adsorption on the same series of catalysts are shown in Fig. 28, where isobars for the various promoter concentrations are represented over a wide range of temperature. If the quantity adsorbed, and the energy of activation involved between 400° and 450° is tabulated against promoter

[1] *J.A.C.S.*, 1934, 56, 2259.

[2] *J. Phys. Chem.*, 1935, 39, 623.

[3] *J.S.C.I.*, 1932, 51, 323.

[4] *P.R.S.*, 1935, **148** A, 186.

concentration (Table 7), it is clear that the amount increases and the activation energy decreases, as promoter is added.

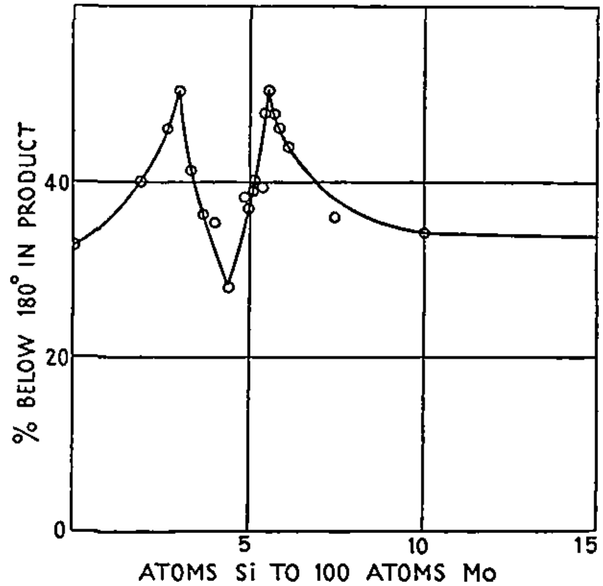


FIG 27. Effect of promoter concentration on high-pressure hydrogenation of tar oil, with molybdenum catalysts.

TABLE 7

Adsorption of hydrogen on promoted molybdenum oxide catalysts

Catalyst, Si *atoms to 100* Mo *atoms*	*c c. adsorbed/100 gm at 450°*	*Energy of activation, K-cals 400–450°*
0·0	9·6	29·0
3·0	22·1	23·9
4·4	22·0	23·5
5·5	38·4	17·6
10·0	50·0	16·9

The adsorption data for hexane, cyclohexane, and benzene have already been given in Fig. 24. It is therefore clear that neither optimum in the high-pressure hydrogenation curve corresponds with maximum adsorption of reactants, but that the minimum point, where retardation of the activity takes place, coincides with maximum hydrocarbon adsorption. It must therefore be concluded that excessive capacity for hydrocarbons will lead to covering of the surface with re-

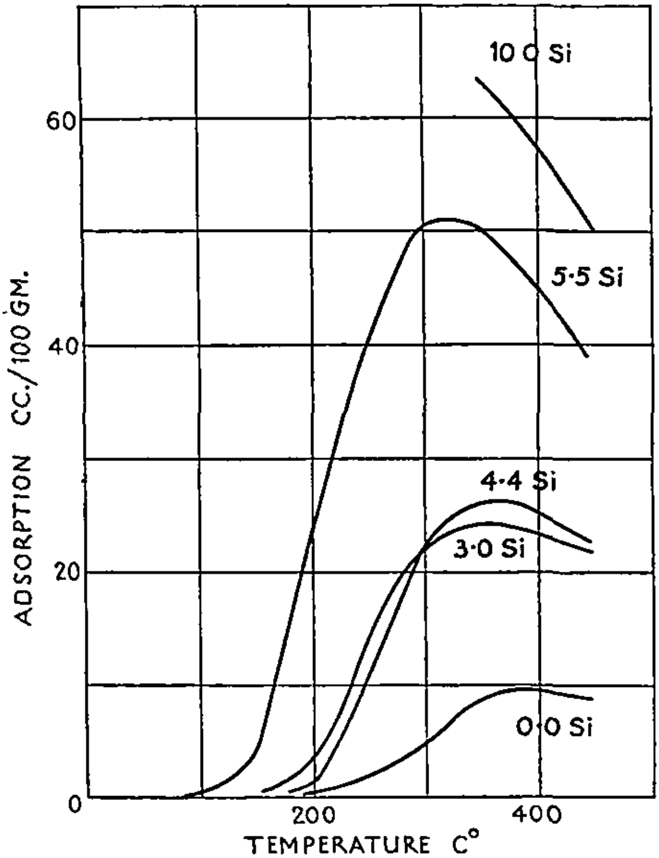


FIG 28. Isobars for adsorption of hydrogen. Effect of promoter concentration on molybdenum catalysts.

action products (which themselves are hydrocarbons of a different type, and all types are similarly adsorbed), so that the ideal proportion between hydrogen and hydrocarbon is disturbed. Further reference to this point is made in the section dealing with retardation (Chapter IV). Additional complications may arise where activated adsorption is of such a character that it becomes indistinguishable from compound formation. A case is found in the synthesis of ammonia on iron or tungsten catalysts,[1] where the adsorption of hydrogen, for instance, was increased by the presence of decomposition products of ammonia leading to the formation of W_xNH or W_xN_2, and where different iron nitrides are known to exist The adsorption of nitrogen, however, still showed the characteristics of activated adsorption.

Simpler cases have been examined in which exchange between deuterium and hydrogen was the reaction involved. Horiuti, Ogden, and Polanyi[2] investigated the reaction between D_2 and C_6H_6 and found that, although hydrogenation of the hydrocarbon does not take place to any appreciable extent at ordinary temperatures in the presence of platinum or nickel, yet exchange reactions do occur under these conditions. This is evidence in favour of the activated adsorption of the hydrocarbon taking place by the formation of hydrocarbon-catalyst complex involving opening of one of the double bonds.

Taylor and his co-workers[3] studied the exchange between deuterium and other compounds containing hydrogen by means of infra-red absorption spectra. With mixtures of methane and deuterium in contact with nickel surfaces deutero-methanes are found in the range 184–305°, equilibrium being reached in 20 hours at the highest temperature but requiring 50 hours at 218° and even longer at 184°. No change could be detected in 90 hours at 110°. It is thus indicated that activated adsorption of methane can occur at much lower temperatures than can be demonstrated by normal adsorption measurements, since it has already been shown that activated adsorption of deuterium itself can take place under similar conditions.[4] This observation strongly supports the original deduction that activated adsorption would proceed at low temperatures with very slow rates, and also supports the suggestion that hydrocarbon fragments are adsorbed on the catalyst surface, as the reaction would otherwise be difficult to explain.

---

[1] Emmett and Brunauer, *J.A C S*, 1934, **56**, 35, Frankenburger and Hodler, *T Farad. Soc*, 1932, **28**, 229, *Z. phys Chem*, 1931, Bodenstein Festb. 593.

[2] *T. Farad Soc.*, 1934, **30**, 663.

[3] *J A C S*, 1935, **57**, 592, 660, 1256

[4] Gould, Bleakney, and H. S Taylor, *J. Chem. Phys.*, 1934, **2**, 362.

Similar results were provided by experiments with iron-alumina-potassium oxide catalysts, such as those used in the synthesis of ammonia, where exchange between D_2 and NH_3 was followed by means of the ultra-violet absorption spectra in the absence of water vapour. No exchange occurred in the absence of the catalyst, but when it was present an exchange could be detected, even at ordinary temperatures, in 23 hours. The occurrence of activated adsorption at much lower temperatures than those indicated by direct measurement is again demonstrated.

In another series of experiments where D_2 was allowed to come into contact with catalysts containing H_2O, such as chromium oxide gel, zinc oxide, zinc chromite, alumina, and platinized asbestos, H_2 was found in the gas; mere displacement of H_2 by D_2 was excluded as in some cases the catalysts had never been in contact with hydrogen. The exchange reaction was also renewed on a zinc oxide surface, where it had already proceeded, on the addition of more H_2O. These reactions are attributed to activated adsorption of D_2 or of H_2O, but the question as to whether both must be activated remains unanswered. Judging from direct measurements with H_2 on alumina, which is only detectable at temperatures above 400°, activated adsorption of water alone or hydrogen alone would appear to be sufficient. This point is more fully discussed in Chapter VII.

Activated adsorption and para-hydrogen conversion.

The magnitude of the energy effects involved suggested that the gas or vapour adsorbed might be held by the catalyst in the form of atoms or radicals rather than as molecules. If this were the case with hydrogen, the catalysts should be effective in bringing about the conversion of para- to ortho-hydrogen, this change only being possible if the gas is in the atomic state. H. S. Taylor and Sherman investigated the effect with catalysts consisting of zinc, manganese, and chromium oxides,[1] and showed that it took place at high temperatures as anticipated, while Emmett and Harkness[2] made similar observations with catalysts used for ammonia

---

[1] *T. Farad. Soc.*, 1932, 28, 247.

[2] *J.A C S*, 1932, 54, 403.

synthesis. In pursuing the idea rather further, the activity of promoted molybdenum catalysts for the conversion of para-hydrogen was compared[1] with their capacity for activated adsorption of hydrogen, but it was found that the velocity of the conversion was unaffected by the presence of promoter while the adsorption of hydrogen was profoundly modified. It must, therefore, be concluded that, although the existence of para-hydrogen conversion in contact with a catalyst is evidence that activated adsorption can occur, yet it cannot be taken as a quantitative means of assessing the activity of the catalyst.[2]

Emmett and Harkness[3] have studied the conversion of ortho- to para-hydrogen with promoted iron and pure iron catalysts. It was found that a catalyst which had been exhausted at 450° and then cooled in helium to —190° was ten or twenty times as active for the conversion at —190° as one which had been cooled in hydrogen. The poisoning effect arising from activated adsorption of hydrogen was more accurately evaluated by the addition of known small amounts of gas at —78° and at 100°. With hydrogen added at —78° the loss of activity was small, but at 100° it was very appreciable, as shown in Fig. 29; these facts are of considerable interest in relation to the observations of the same investigators on the different types of adsorption of hydrogen on iron surfaces (see p. 33).

Farkas[4] has compared the exchange reaction between ammonia and deuterium with the ortho-para-hydrogen conversion on an iron catalyst, which was found to contain H_2 even when apparently completely de-gassed, unless deposited by evaporation from iron wire at 1,100–1,200°. The conversion reaction took place under conditions where no exchange could be observed, and had a lower energy of activation, but was strongly retarded by ammonia. The rate of the exchange reaction was independent of the pressure of ammonia but proportional to the square root of the deuterium pressure,

---

[1] Griffith and Hill, *P R.S.*, 1935, **148** A, 202.

[2] See also Howard, *T. Farad. Soc.*, 1934, **30**, 285; H. S. Taylor, *J.A C.S*, 1935, **57**, 1251.

[3] *J.A.C.S.*, 1935, **57**, 1624.

[4] *T. Farad Soc.*, 1936, **32**, 416.

and the mechanism of the process was not as simple as might be anticipated. In conjunction with other evidence concerning the behaviour of ammonia on iron or tungsten surfaces (see p. 49) it was concluded that the exchange involved interaction of deuterium with an adsorbed $—NH_2$ fragment.

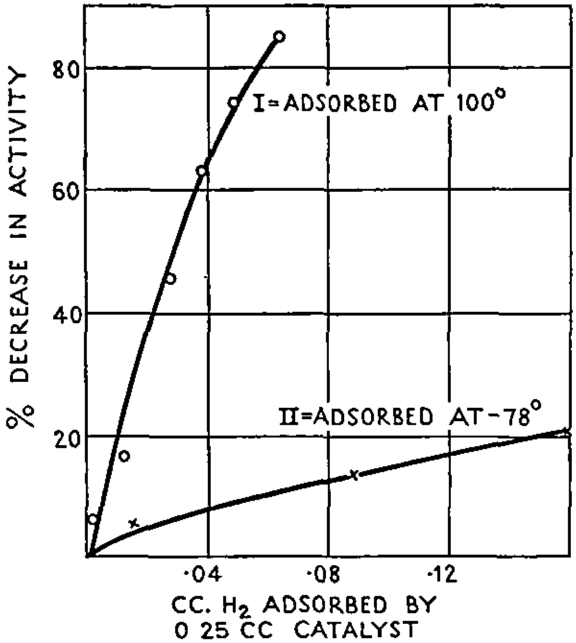


FIG. 29. Effect of adsorbed hydrogen on ortho-hydrogen conversion, by iron catalyst.

The subject of the isomers and isotopes of hydrogen is dealt with fully by Farkas's book, *Ortho-hydrogen, Para-hydrogen, and Heavy Hydrogen,*[1] which should be consulted for further details.

The interaction of carbon and hydrogen.

The case of the conversion of solid carbon into gaseous compounds is of particular interest as the solid reactant in this case is the catalyst for the reaction. The most fully investigated examples of this type are the production of methane from carbon and hydrogen, and the combustion

---

[1] Cambridge, 1935.

of carbon in oxygen, but the interaction of carbon with steam or with carbon dioxide may well prove to be exactly parallel.

Kingman[1] showed that activated adsorption of hydrogen occurred on charcoal, and Barrer[2] has studied the behaviour of hydrogen and methane in contact with non-graphitic charcoal. The adsorption of hydrogen was found to follow the Langmuir equation whenever equilibrium was really established; the isobars between 10^{-4} and 100 cm. pressure were all of the same form and contained a maximum in the highest pressure curve, showing that equilibrium had not been established in the time employed for the measurements at lower temperatures (Fig. 30), which is a characteristic feature of activated adsorption. Calculation of the heats of adsorption showed that the mean value was largely independent of the amount taken up, as illustrated in Table 8 for the temperature range 1,171–1,223° K. The striking feature about this observation is that the mean value is very close to the known figure of 48,000 cals. for hydrogenation of the triple bond in acetylene.

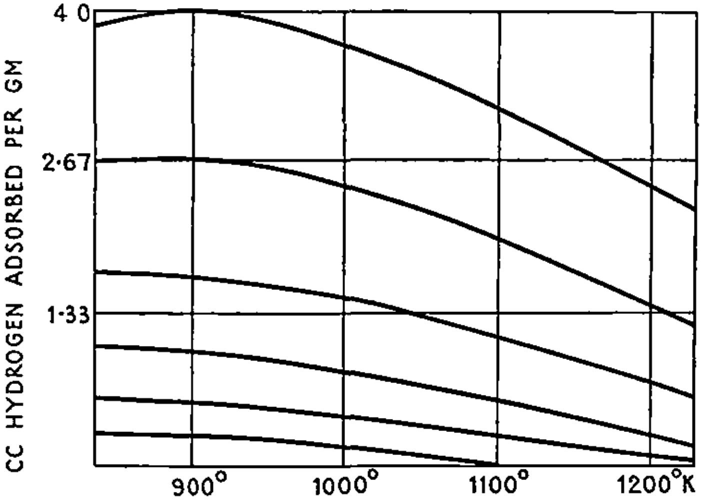


FIG. 30. Adsorption isobars for hydrogen on charcoal.

---

[1] *T. Farad. Soc*, 1932, **28**, 269.

[2] *P R.S.*, 1935, **149** A, 253

TABLE 8

Heat of adsorption of hydrogen on charcoal

c.c adsorbed by 5·9 gm	*Temp. coefficient*	*Heat of adsorption cals /gm. mol.* H_2
0·1	2·48	49,950
0·316	2·55	51,460
1·10	2·53	50,030
3·16	2·80	56,630

The energy of activation at high temperatures was found to increase as the amount of gas adsorbed was increased, as indicated by Fig. 31. The actual measurements of velocity of adsorption were also useful in showing that diffusion effects as well as activated adsorption came into play at higher temperatures. The rate of a diffusion will depend on the square root of the temperature, but the relation between activated adsorption and temperature is exponential. The two curves *A* and *B* of Fig. 32 show the calculated velocity constants which would be given for the two processes, while the observed points indicate that a change from one type to the other takes place as the temperature is raised.

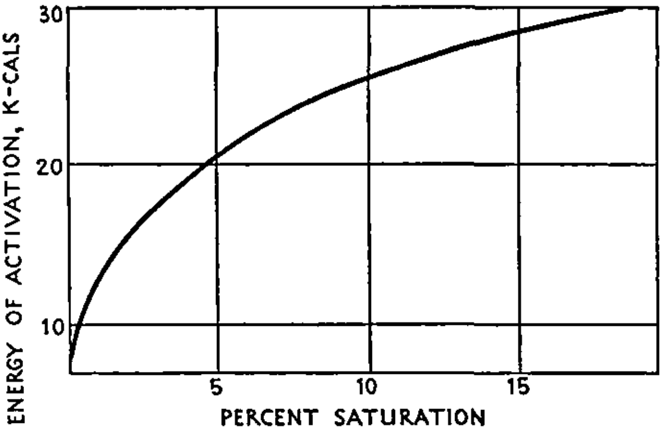


FIG. 31. Energy effects during adsorption of hydrogen by charcoal.

The slow establishment of the methane equilibrium was detected when hydrogen was left in contact with the charcoal, but the solid which contained adsorbed hydrogen did not react with oxygen at room temperature. The adsorbed hydrogen, in fact, behaves in every respect just like the —C-H link in a hydrocarbon; and the general character of the change is very similar to that observed with oxygen and charcoal.

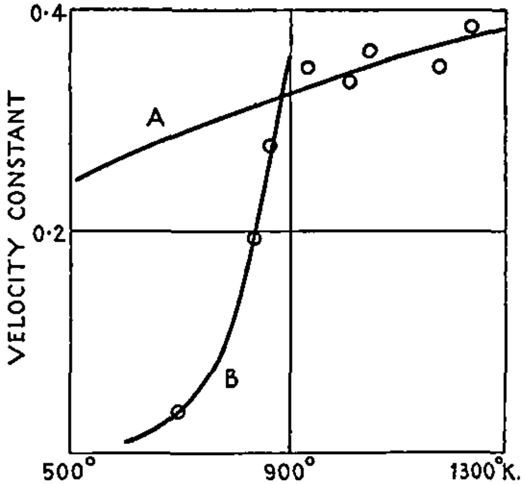


FIG. 32. Relation between calculated and observed velocity constants.

A, calculated for diffusion.
B, „ activated adsorption.
Experimental points marked.
Adsorption of hydrogen on charcoal

The combustion of carbon.

Rhead and Wheeler's experiments on the combustion of carbon[1] are of great interest in connexion with the adsorption of oxygen. They admitted air or oxygen to carbon which was heated in a porcelain tube, and measured the rate of disappearance of oxygen at different temperatures. From the curves they obtained (Fig. 33) it was evident that the rates were comparable when the temperature was altered, although the total amounts involved were different. The oxygen which was thus adsorbed was very firmly retained at temperatures up to about 900°, and only by heating as well as evacuation could it be removed in the form of an oxide of carbon. Rhead and Wheeler, therefore, postulated the existence of a complex

---

[1] *J.C.S.*, 1913, 103, 461.

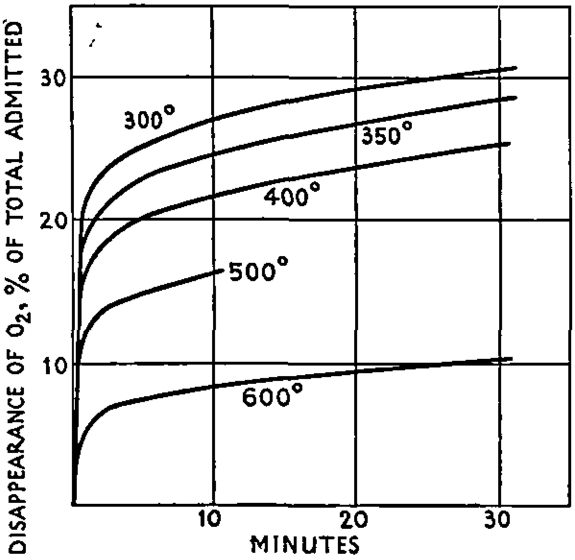


Fig 33. Rate of oxygen adsorption by charcoal.

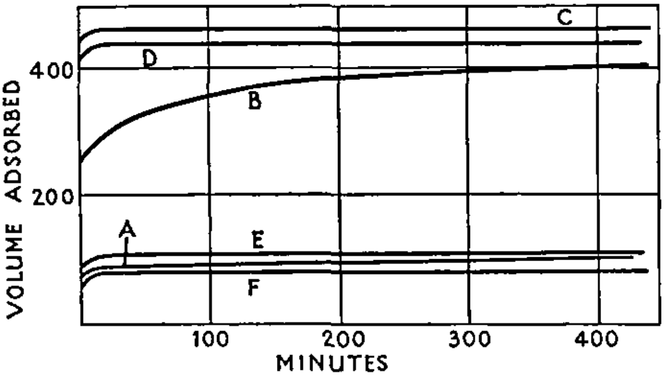


Fig. 34. Rates of adsorption on charcoal.

A, oxygen.
B, nitric oxide.
C, nitrous oxide
D, carbon dioxide.
E, carbon monoxide
F, nitrogen.

C_xO_y on the surface, and supposed that the ratio of carbon monoxide to dioxide that was formed under any particular conditions depended on the intensity of the reaction by which the complex was produced.

Further investigations by Shah[1] provided a more detailed description of these phenomena. Sugar charcoal was examined as an adsorbent for oxygen, nitrous and nitric oxides, nitrogen and oxides of carbon, and results illustrated in Fig 34 were obtained, equilibrium being rapidly attained except in the cases of oxygen and nitric oxide; the curves for the latter show the characteristics of activated adsorption On evacuation, nitrous oxide, nitrogen, and carbon oxides were given off practically unchanged at 0°, but only part of the oxygen or the nitric oxide could be recovered at that temperature. On raising the temperature varying amounts of gas containing oxides of carbon were liberated in the manner shown by Fig. 35 and in Table 9. It was thus concluded that oxygen was retained as a complex which broke down at about 280°, but that nitric oxide was slowly decomposed even at ordinary temperatures, the oxygen part of the molecule being retained by the carbon.

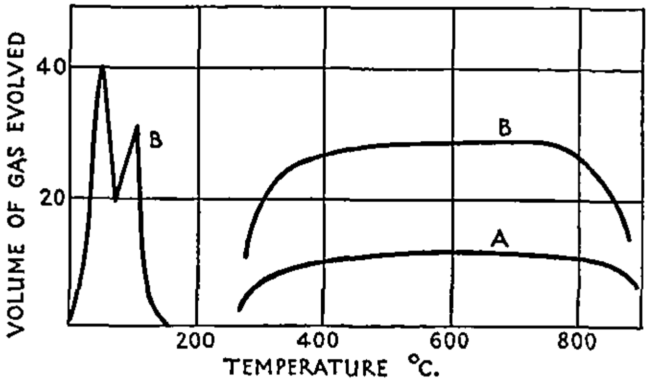


FIG. 35. Gases recovered from charcoal.
A, experiments with oxygen.
B, „ „ nitric oxide.

In view of the information now available with respect to activated adsorption, these results can readily be interpreted as a case exactly similar to the behaviour of hydrogen with charcoal.

The presence of small amounts of impurities has a large influence on the course of the reaction between carbon and

---

[1] *J C S.*, 1929, 2663, 2676.

oxygen. Langmuir[1] showed that, when oxygen came into contact with a clean carbon surface at 950°, carbon dioxide alone was produced, while other investigators, as already mentioned, detected the monoxide as well Lambert[2] has accounted for these differences by the effect of iron which is associated with all but the very purest forms of carbon. Graphite and diamond gave results in strict accordance with those of Langmuir, but a second process, involving the breakdown of the surface layer, only occurred with charcoals containing iron.

TABLE 9

C.c.s of gas recovered from charcoal, after adsorption of oxygen or nitric oxide

Temp of evacuation	*Oxygen adsorbed*			*Nitric oxide adsorbed*			
	CO_2	CO	O_2	CO_2	CO	NO	N_2
0° C.	.	..	133 5	4·3	..	130 8	96 4
25	..	.	..	2 2	..	10 9	1·9
50	.	.	.	9 8		27·0	5 0
75	0 8	0 0		5·8	.	12·4	1·4
100	..	.	..	12 1	..	16 4	2·8
125	.	..	.	2 3		1 8	0 6
150		.		1 1		0 1	0·1
300	5 2	2 2	..	15 6	5 0	.	1 0
450	4 6	5·7		12 4	15 3	..	0 7
600	2 8	7 7	..	7 0	20 6	.	0 4
750	0 5	9 7	..	0 9	27 5		0 4
950		5 1	.	..	6 0	.	5 8

During the interaction of oxides of carbon and of steam with carbon similar processes are undoubtedly involved, but a feature of additional interest arises in cases where the conversion of carbon into its oxides is accelerated by the addition of inorganic substances to the coke or charcoal which is used. This was found to occur chiefly with sodium carbonate, calcium oxide, and iron oxide.[3] In Fig. 36, for example, is shown the effect of additions to the coke on the reduction of carbon dioxide at different temperatures, and in Fig. 37 are given some parallel results for the interaction of carbon and steam.

---

[1] *J A C S.*, 1915, 37, 1154.

[2] *T. Farad. Soc*, 1936, 32, 452.

[3] Cobb and others, *Gas J.*, 1927, 178, 895, *Inst Gas Eng*, 1927.

The similarity in form of the two sets of curves is very striking and suggests a close relation between the reactions concerned in each case.

The acceleration caused by iron and calcium oxides was later considered by Askey and Doble[1] to be due to displacement of alkali already present in the inherent ash of the charcoal. The experiments of Fox and White[2] on the products obtained by the interaction of sodium carbonate and carbon indicated that the reaction involved was

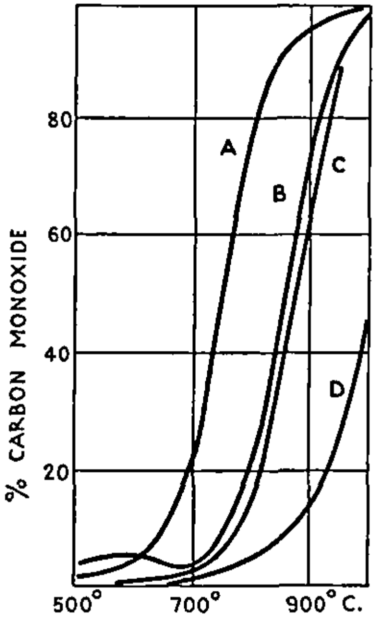


FIG. 36 Reduction of CO_2 by coke

A, Na_2CO_3 coke.
B, Fe_2O_3 „
C, CaO „
D, Untreated coke.

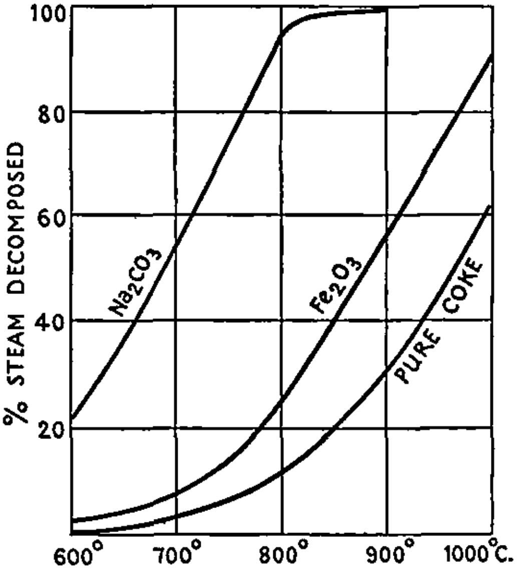


FIG. 37. Effect of temperature on different cokes, reacting with steam.

$$Na_2CO_3+2C = 3CO+2Na,$$

which was followed by the formation of more sodium carbonate in the presence of steam and carbon dioxide. This series of changes presumably occurs more rapidly than the

---

[1] *Fuel*, 1935, **14**, 197.

[2] *Ind. Eng. Chem.*, 1931, **23**, 259.

direct gasification of carbon. The present case, therefore, must not be considered as an example in which the addition of a promoter increases the rate at which the catalyst itself is involved in a reaction, but at the same time a closer study of the velocity of adsorption of carbon dioxide and steam on carbon surfaces would undoubtedly provide information of very considerable interest.

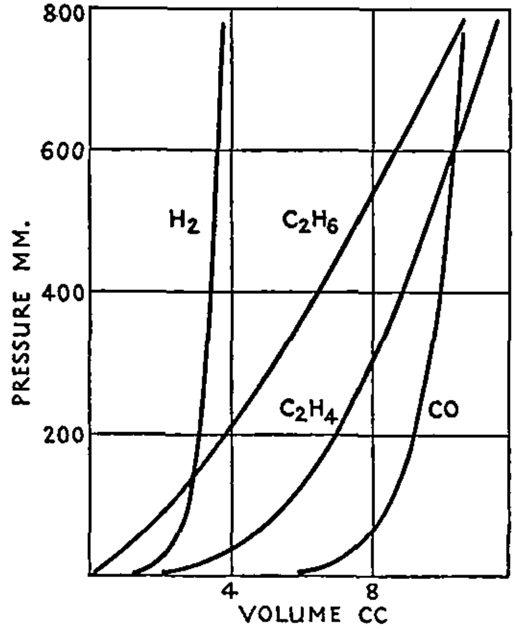


FIG 38. Adsorption on 117 gm. of copper at 0°.

Effect of pressure on adsorption.

The general form of isotherm for adsorption at low temperatures on substances such as copper (Fig. 38) is described by Pease,[1] and suggests that the surface is not always completely saturated with the adsorbed material at pressures below atmospheric, and that therefore the effects might often be altered or magnified by raising the pressure to several hundred atmospheres. Experimental evidence on this point is very scanty in spite of the rapidly increasing application of high pressure to chemical processes. But the results of

---

[1] *J.A.C S.*, 1923, 45, 2235, 2296

Frohlich[1] for the adsorption of methane on charcoal, given in Fig. 39, do indicate an upward drift of the isotherm.

The appearance of the isotherms obtained by McBain and Britton[2] for the adsorption of nitrogen, nitrous oxide, and ethylene on sugar charcoal for pressures up to 60 atmospheres was similar. It was observed that true reversible adsorption took place in accordance with the Langmuir equation. In the experimental determinations a correction for buoyancy became important at the higher pressures, which introduced some uncertainty as to the absolute values involved owing to lack of knowledge of the true density of the charcoal. In view of the unique structure of charcoal it is doubtful whether any general conclusions can be drawn from these results, as to the behaviour of other types of contact substances.

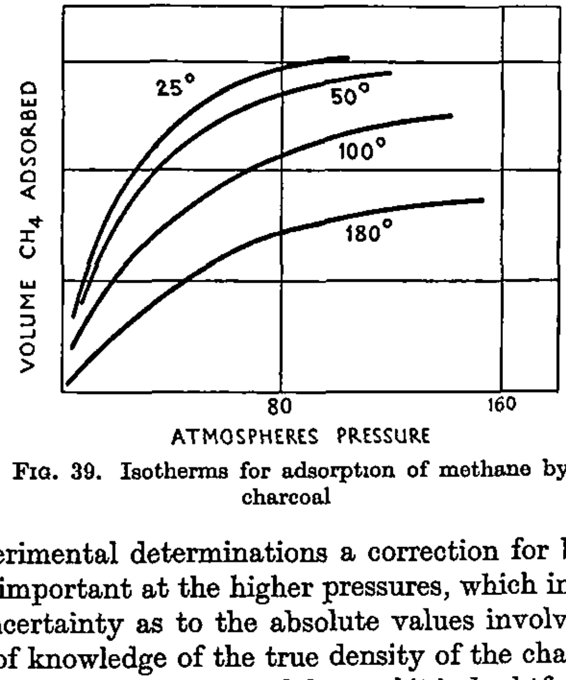


FIG. 39. Isotherms for adsorption of methane by charcoal

The observations of Frankenburger and Hodler[3] concerning the adsorption of ammonia on tungsten showed that a three-stage isotherm existed (Fig. 40) in which the high-pressure stage was attributed to condensation of ammonia on the surface. Owing to the slow upward drift observed in this range the true equilibrium values were not determined, but the use of considerably greater pressures in measurements of

---

[1] *Ind. Eng. Chem.*, 1930, **22**, 1058.

[2] *J.A.C.S.*, 1930, **52**, 2198.

[3] *T. Farad. Soc*, 1932, **28**, 229

this type would be of much interest if they were carried out at rather higher temperatures.

Emmett and Brunauer[1] have attempted such determinations in the case of nitrogen adsorption on promoted iron catalysts at pressures up to 50 atmospheres. The method employed was to saturate the surface with nitrogen at the desired temperature and pressure, then to cool the whole system, release the pressure, and displace the adsorbed nitrogen with a stream of hydrogen at 450°, which led to its appearance as ammonia There are, however, serious objections to the use of such indirect methods until more absolute data are available concerning the effects of pressure, and the position is clearly complicated in the system under review by the existence of iron nitride.

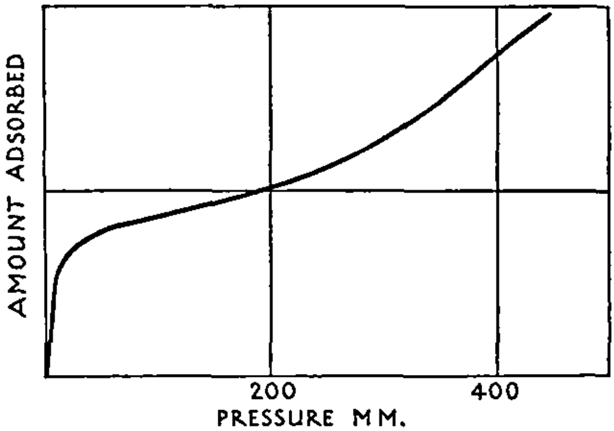


FIG. 40 Isotherm for ammonia at 20°, adsorbed by tungsten.

Simultaneous adsorption of more than one gas.

Only very limited experimental evidence is available as to the simultaneous adsorption of mixtures. In cases where both reactants are being considered it is obvious that actual determinations cannot be carried out at temperatures at which the reaction takes place, and in general the qualitative information which is provided by a study of retardation

---

[1] *J.A C S*, 1934, 56, 35.

(pp. 101, 153) is of much more value than adsorption measurements which have been made at ordinary temperatures.

Mention may be made, however, of a few determinations which have been described, in order to demonstrate the effects to be expected Frankenburger and Hodler[1] found that the adsorption of hydrogen on tungsten was not affected by the presence of nitrogen, and, in the case of mixtures of carbon dioxide and nitrous oxide, Richardson and Woodhouse[2] observed similar effects. Such examples are, however, comparatively rare, and considerable interference generally occurs, as with carbon monoxide and hydrogen adsorbed on copper catalysts which were investigated by Hurst and Rideal.[3]

---

[1] *T Farad. Soc.*, 1932, **28**, 229.

[2] *J A C.S.*, 1923, **45**, 2638.

[3] *J.C.S.*, 1924, **125**, 694.

CHAPTER III

PROMOTERS AND CARRIERS

WHEN a second substance is added to a one-component catalyst a very large number of different consequences may arise. The individual cases will be considered in this and the following chapter under the general classification shown below.

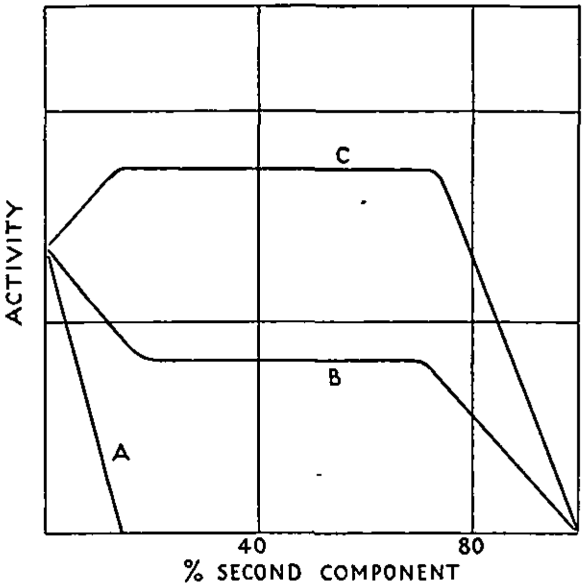


FIG. 41. Compound formation in two-component catalysts.

A, the compound is inactive.
B, „ „ less active than first component.
C, „ „ more active than first component.

For simplicity of treatment the discussion will primarily be restricted to conditions where the second component has itself little catalytic effect.

A. Compound formation.

If interaction between the two components of the catalyst can occur there are three possible consequences which are illustrated in Fig. 41. If the compound has no catalytic effect the result will be a rapid fall in the activity, exactly similar to that produced by a catalyst poison, as shown by curve *A*. On the other hand the new compound may have a positive effect which is either lower (curve *B*) or higher (curve *C*) than that of the original catalyst; in either case, excess of the second component will eventually lead to complete loss of activity. Any of these curves may in practice appear to have a more rounded form than those shown in the ideal cases illustrated.

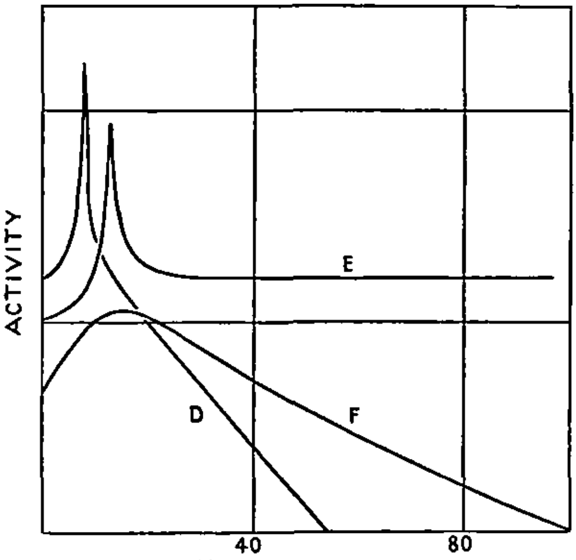


FIG. 42 Examples of promoter action.

D, the promoter itself is inactive
E, „ „ has a positive activity.
F, the experimental data are insufficient to reveal the true shape of curve.

B. Promoter action.

When the activity-concentration curve rises to a very sharp maximum and then falls steeply again (Fig. 42) the case is one of true promoter action, and it is proposed to restrict the term to this particular set of conditions. The fall beyond the optimum may be to zero, or to a steady positive activity as indicated by the two alternative curves *D* and *E*. If measurements are not made at sufficiently close intervals of promoter concentration the real shape of these curves will be masked and the results will be of the type shown by line *F*.

C. Carrier action.

In Fig. 43 three alternative consequences of carrier action are illustrated. Curve *G* shows the simplest of these in which straight dilution occurs. The activity of the catalyst may, however, remain unaltered by the addition of quite large amounts of carrier, until eventually it falls as indicated in curve *H*; this may be termed delayed dilution. When the addition of a carrier leads to a rise in activity, as represented by curve *J*, the effect is due to prevention of physical change which would otherwise lead to a lowering of the catalytic power.

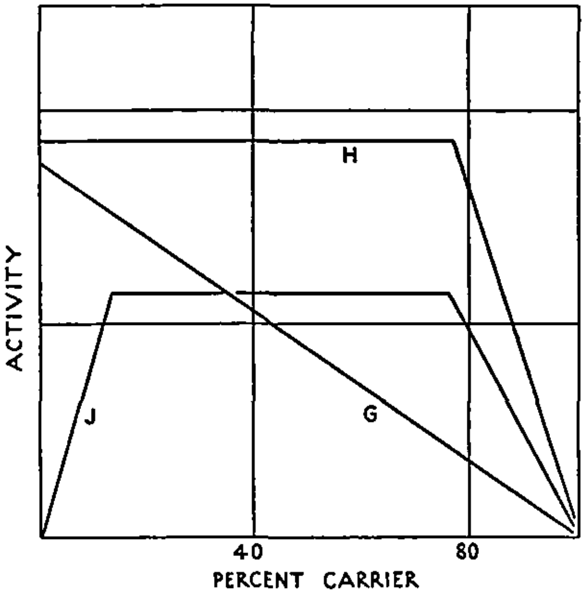


FIG. 43. Types of carrier action.
G, straight dilution.
H, delayed dilution.
J, prevention of sintering.

When the second component is also an active catalyst the foregoing possibilities will all be multiplied. The simplest case will be that in which there is no mutual effect, but there are obviously opportunities for poisoning of component *X* by component *Y* simultaneously with a promoting effect of *X* on *Y*. An extreme case may also arise in which neither component alone has any catalytic effect, but both together are very useful.

Examples of these cases will be described in more detail.

Apparent poisons.

The case of true poisoning or retardation, caused by impurities in the reactants or by adsorption of a reactant or reaction product, is described in the following chapter. Apparent poisoning may occur with two component catalysts from entirely different causes, the chief of which is compound formation. It is evident that if a particular compound is formed by the addition of a second substance to the original catalyst, and that compound is stable under the conditions of experiment, it will exert its own specific catalytic effect. When this effect is nil the original activity will be destroyed.

A second cause of apparent poisoning is due to an alteration in the state of oxidation of a catalyst caused by the addition of a second substance. In the case of titanium dioxide, for example, the presence of small quantities of alkali suppresses the reduction by means of hydrogen, and the catalyst activity, for the decomposition of hexane, is greatly affected. The addition may alternatively lead to further reduction than occurs with the pure catalyst, so that an active oxide is converted into one with a much lower effect. According to Kobozev, Jerofejef, and others[1] the reduction of an oxide such as Fe_3O_4 is affected by changes in the surface tension of the catalyst, and this in turn is altered by the presence of a promoter; influences of this type can also be expected to have a harmful, as well as a beneficial, result. Further reference to this point will be made in discussion of changes in active surfaces which occur during use (see Chapter V).

Compound formation.

The extensive researches of Mittasch and his co-workers on two-component molybdenum catalysts for ammonia syn-

---

[1] *Act. Physicochim.*, 1934, **1**, 483.

thesis[1] illustrate the effects which may arise when compound formation takes place. The addition of nickel in amounts greater than required to form the compound NiMo gave catalysts which completely lost their activity in long tests,

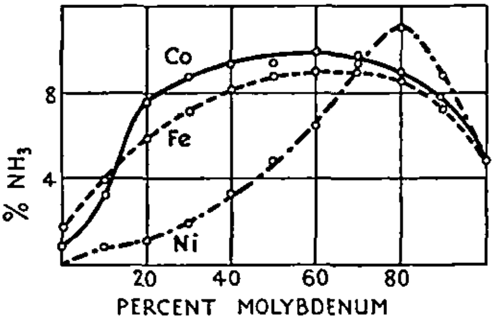


FIG. 44. Activity of mixed catalysts for ammonia synthesis, after 24 hours.

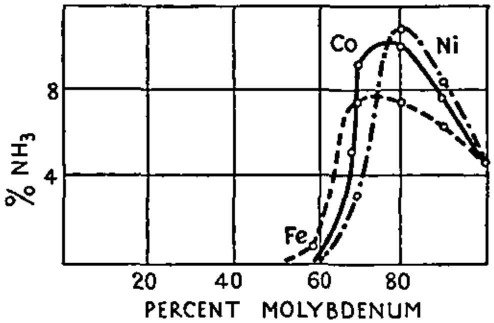


FIG 45. Activity of mixed catalysts for ammonia synthesis, after 6 weeks.

whereas those mixtures in which excess molybdenum, over the quantity required to combine with the nickel, gave catalysts of high and persisting activity which contained molybdenum nitride. The behaviour of cobalt and iron was found to be similar, as shown in Figs. 44 and 45, but the addition of copper, silver, chromium, and tungsten was quite different, no compounds being produced and activity-composition curves as shown in Fig. 46 being obtained. In the case of

---

[1] *Z phys. Chem*, 1931, Bodenstein Festb., 574; *Z Elektrochem*, 1930, 36, 567, 690.

copper-zinc catalysts used for the synthesis of methanol, the expansion of the copper-crystal lattice, which has been observed by Frohlich and others,[1] is attributed by Frost[2] to the formation of brass, and this expansion of the crystal was found to coincide closely with catalytic activity. On the other hand it was found that the addition of promoters to zinc oxide, for use as a methanol catalyst, did not affect the crystal structure It therefore appears that X-ray investigation will reveal the existence of compound formation, or mixed crystals, but not of true promoter action.

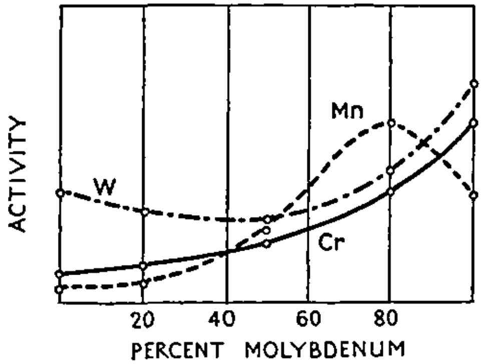


FIG 46. Activity of mixed catalysts for ammonia synthesis.

A further case of compound formation has been found with molybdenum oxide catalysts used in the conversion of phenol to benzene [3] When sodium oxide was added the catalyst had no activity at all, corresponding with the example of apparent poisoning discussed above, while if cerium oxide was used over a wide range of concentration, the activity was always identical with that given by cerium molybdate separately prepared. Although reduction of the molybdic acid took place, as shown by the change in colour of the catalyst before and after use, it is evident that the link Mo-Na and Mo-Ce still persisted at 450° in the presence of phenol, water, hydrogen, and benzene; whereas it is interesting to note that such salts of molybdic acid were completely dissociated in contact

---

[1] *Ind Eng. Chem*, 1929, **21**, 109 [2] *Act. Physicochim.*, 1934, **1**, 511.

[3] Griffith, unpublished data

with hexane at 500° (see p. 74). Similar specific effects of compound catalysts have been observed by Kingman and Rideal[1] with heteropoly acids containing molybdenum, again when used for the production of benzene from phenol.

Promoters.

The fact that the activity of a catalyst could be considerably increased by the addition of small amounts of other substances was emphasized by early patents of the Badische Anilin und Soda Fabrik,[2] and since that time has been described in a very large number of patent specifications. Little experimental work on the subject is, however, recorded in detail, and a large proportion of the information available is undoubtedly misleading. A review of the literature by Pease and H. S. Taylor[3] served to clarify the position and suggested a definition of promoter action in the following phrase: 'Cases in which a mixture of two or more substances is capable of producing a greater catalytic effect than can be accounted for on the supposition that each substance in the mixture acts independently and in proportion to the amount present.' With certain limitations this definition will still serve well, Rideal and Taylor[4] suggested that it should be restricted to the effects produced by relatively small quantities of a material which itself was inert or of negligible catalytic activity in the reaction concerned.

The influence of small additions of cerium oxide on the catalytic activity of thoria for the oxidation of electrolytic gas was described by Swan,[5] and the Harger-Terry process for catalytic combustion of carbon monoxide required the presence of 2·5 per cent of cerium oxide added to iron oxide.[6]

Medsforth[7] investigated the reduction of oxides of carbon by hydrogen with supported nickel catalysts containing varying amounts of oxides as promoters. The effects were very similar with either carbon monoxide or dioxide, but the

---

[1] *Nature*, 1936, **137**, 529.

[2] B.P. 19249/10, B.P. 27963/13, B P. 2306/14, &c.

[3] *J. Phys. Chem*, 1920, **24**, 241.

[4] *Catalysis in Theory and Practice*, 1926, p. 102.

[5] *J C S.*, 1924, **125**, 780.

[6] B P. 127609/17.

[7] *J.C.S*, 1923, **123**, 1452.

extent of increase of activity and the position of maximum effect depended on the particular promoter employed, as shown in Fig. 47. It was concluded that the optimum promoter concentration varied with each substance, and with the method of preparation, but considerable difficulties were certainly encountered owing to the use of supported catalysts,

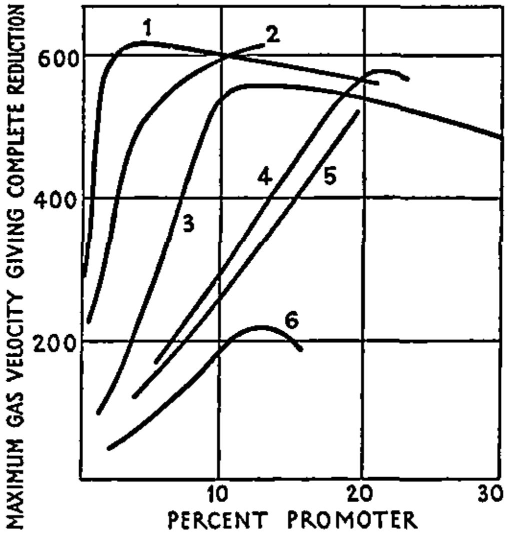


FIG. 47. 1, Ce_2O_3 promoter, reduction of CO
2, ThO_2 „ „ CO
3, ThO_2 „ „ CO_2.
4, BeO „ „ CO.
5, BeO „ „ CO_2.
6, Mo_2O_3 „ „ CO.

as these were obtained by soaking pumice with solutions of mixed nitrates.

Similar striking increases in activity during the early stages of promoter addition were observed by Hurst and Rideal[1] in the case of copper catalysts containing palladium, which were used for the selective combustion of carbon monoxide in admixture with hydrogen. Seven different mixtures were prepared by precipitation of the mixed nitrates with alkali, and it was found that the presence of the promoter did not affect the position of the optimum temperature for the selective effect, which was about 175° in every case; this was also

---

[1] Ibid., 1924, **125**, 685.

the temperature at which cupric oxide was formed by the interaction of copper and oxygen, cuprous oxide being produced at lower temperatures. The relation between promoter concentration and oxidation of carbon monoxide is shown in Fig. 48.

Armstrong and Hilditch[1] used nickel catalysts containing promoters, which were obtained by precipitation of mixed solutions with sodium carbonate, followed by reduction of the oxides in hydrogen. The reduced catalyst was cooled in carbon dioxide and then dropped into cotton seed oil, its activity being tested by the absorption of hydrogen at 180° during 1 hour, the change in iodine value of the product being used as a criterion of the extent of reaction. In the curves of Fig. 49 the decrease in iodine value is plotted against the promoter concentration, and it can be seen that a sharp initial rise in activity is followed by an almost equally rapid fall.

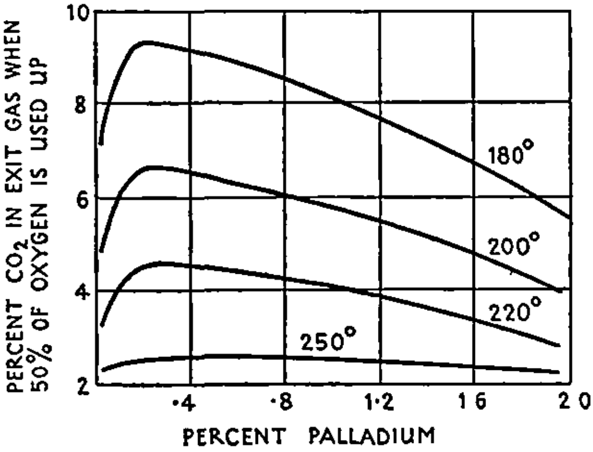


Fig. 48.

Rideal and Taylor[2] commented on the position with regard to promoter action at that time that 'most of the statements concerning promoter action by added substances have no information which would indicate what the optimum concentration of promoter is for the given reaction', and they concluded that 'around the optimum concentration, marked

---

[1] *P R S*, 1923, **103**A, 586

[2] *Catalysis in Theory and Practice*, p. 113.

changes in velocity with change in concentration of promoter would not be expected'.

Later determinations by Scott and Leach[1] of the activity of cobalt catalysts for the oxidation of ammonia showed that the addition of promoter led to a sharp rise, followed by a slow fall from the maximum, while Goggs[2] obtained a closer

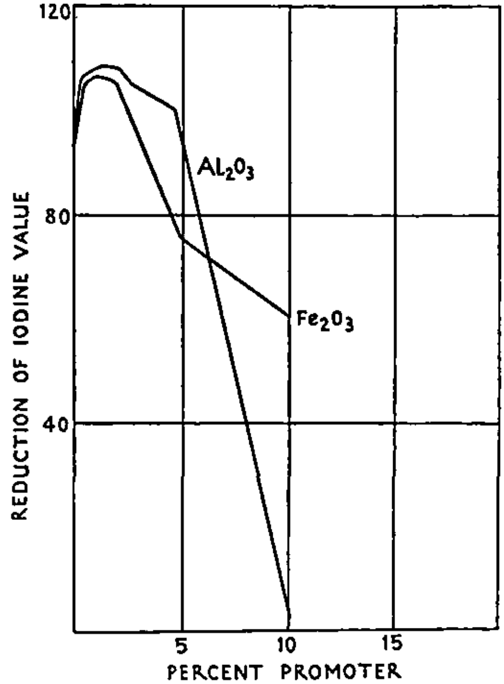


FIG. 49.

approach to the conception of a critical promoter concentration in the case of the effect of cerium oxide on thoria catalysts used to accelerate the combustion of carbon monoxide. These are given in Table 10, where the range in which optimum activity is produced is evidently fairly narrow. None of these examples, however, really coincides with the ideal promoter curve postulated at the beginning of this chapter.

Evidence for the real existence of such curves is now available from the data of Griffith and Plant[3] on the effect of silica

---

[1] *Ind Eng Chem.*, 1927, 19, 170.

[2] *J.C S*, 1928, 2667.

[3] *P.R.S.*, 1935, 148A, 191.

concentration on the activity of molybdenum oxide catalysts used in the decomposition of hexane and cyclo-hexane. In Fig. 23 the activity is plotted against promoter concentration expressed as a ratio of atoms of silicon to 100 atoms of molybdenum; this method was adopted as an absolute means of comparison which was independent of the precise state of oxidation of the metal. It will be appreciated that the mixtures were now being investigated within very fine limits, and that if wider variations in the concentration of silica had been inspected the real form of the curve might well have been obscured.

TABLE 10

Combustion of carbon monoxide with ThO_2 *catalysts prepared from mixed nitrates by precipitation with oxalic acid.*

Per cent. CeO_2	*Rate of* CO_2 *formation (mean of several runs)*
0·0	1·30
0·5	9·0
0·8	14·0
0·96	18·0
1·2	16·2
3·0	4·3

Use of alternative promoters.

A much more thorough investigation of this aspect of promoter action was made by Griffith[1] in a comparison of the effects produced by a large number of different promoters. Molybdenum oxide was again used for the decomposition of hexane, and the optimum concentration of oxides of chromium, sodium, cerium, aluminium, barium, boron, silicon, and thorium, and of metallic iron, lead, and copper, was determined. The promoters were added either as colloids, or were precipitated *in situ* by the addition of ammonia to the molybdic acid to form just sufficient ammonium molybdate to react with a soluble salt of the promoter element. The promoter curves obtained are shown in Figs. 50, 51, and 52, and the fact that the effects are not due, in this case, to compound formation is clearly established from the very similar shape of every curve.

---

[1] *Nature*, 1936, 137, 538.

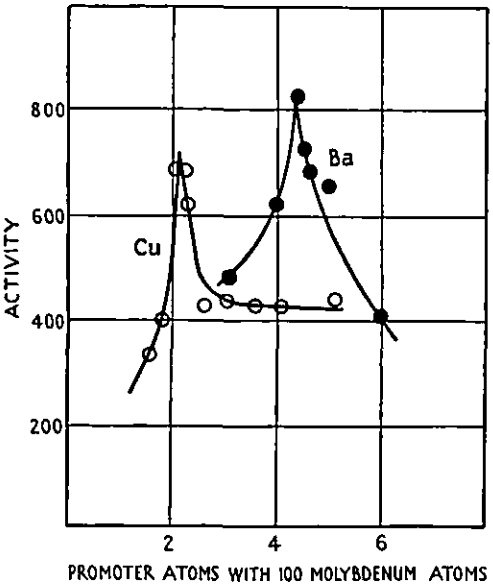


FIG. 50 Effect of promoter concentration on activity of molybdenum oxide catalysts for hexane decomposition at 500° (1)

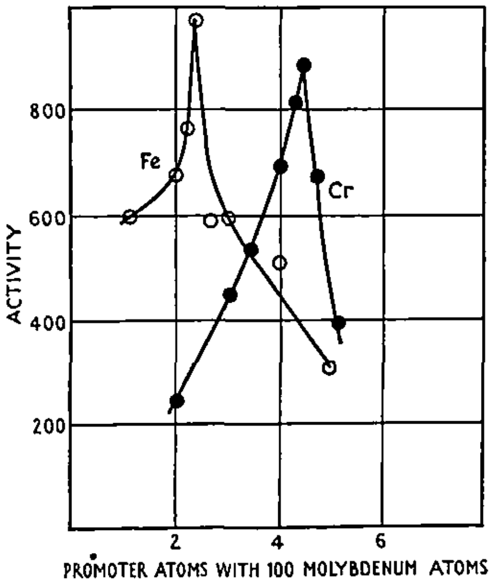


FIG 51. Effect of promoter concentration on activity of molybdenum oxide catalysts for hexane decomposition at 500° (2).

By comparison of these results, shown in Table 11, it is found that the ratio of promoter element to molybdenum, which gives greatest catalytic activity, is independent of the particular oxide used; that is, the optimum promoter concentration is a function of the catalyst and not of the promoter. From the data already presented with respect to the adsorption of three different types of hydrocarbon on molybdenum oxide-silica mixtures, the concentration is also shown to be independent of the particular hydrocarbon which is undergoing decomposition. When, however, the promoter which is used is a compound that is converted into the metal under the conditions of experiment, the atomic ratio required to give the maximum effect is only half that which is necessary for an oxide promoter. The ratè of rise and fall, the maximum which is reached, and the final value given with excess of promoter are found to depend somewhat on the particular promoter which is being used.

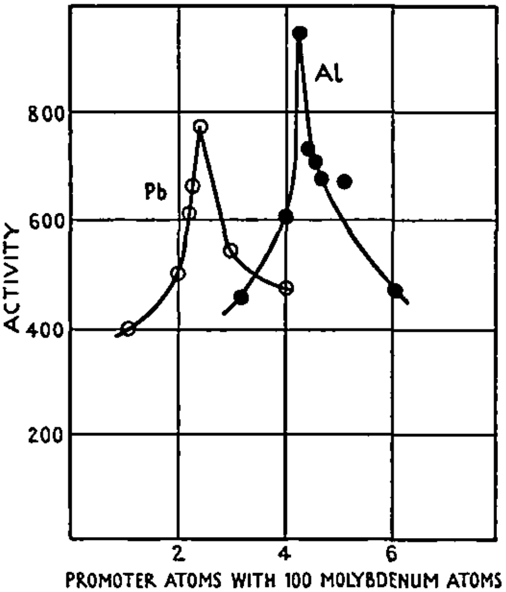


Fig. 52. Effect of promoter concentration on activity of molybdenum oxide catalysts for hexane decomposition at 500° (3).

TABLE 11

Optimum promoter concentration with molybdenum oxide catalysts, ratio promoter atoms to 100 Mo *atoms*

Promoter element	*Atoms*	*Activity*
Na	4·3	694
Cr	4·3	898
Ce	4·25	618
Al	4·6	950
Ba	4·3	833
B	4·3	844
Th	4·5	613
Si	4·3	825
Fe	2·1	1,000
Cu	2·1	687
Pb	2·35	744

These facts suggest that the promoter is functioning by means of valency bonds, and that a metal can be effective with respect to two active centres simultaneously.

One other fact of importance has also been revealed during this investigation. The equivalence of all the oxide promoters suggested that addition of a second promoter to a mixture which already contained the optimum amount of a first promoter, would lead to a lowering of activity. This, in fact, proved to be the case, and it is suggested that, in all cases of straightforward promoter action where no complications due to compound formation can occur, better results should never be obtained by the use of multiple-promoted catalysts than could be reached with a single promoter. If the true optimum has not been found for the first, it is obvious that the further addition of small traces of a second substance may actually give enhanced activity, and this is probably the explanation of cases of this type which are on record.

Larson and Brooks[1] studied the effect of mixed promoters on iron catalysts used for the synthesis of ammonia, and found that if the oxides selected were closely related chemically the combined effect was purely additive, but that if they were not similar a greater effect was often obtained. Unfortunately, however, these mixtures were prepared

---

[1] *Ind. Eng. Chem.*, 1926, **18**, 1305.

mechanically, and no information is included as to the proportions of the individual components. Data of Almquist and Crittenden[1] also showed that enhanced effects could be produced by the simultaneous presence of two dissimilar oxides, but these are again open to the same objections.

It will be appreciated, however, that complications due to carrier action, simultaneous catalysis, compound formation, and other factors may produce greater activity than in singly promoted catalysts, but that such occurrences do not alter the discussion of the ideal case. It may be noted at this point that Cassel[2] has suggested that promoter action takes place when the main component adsorbs one reactant, and the promoter another. This suggestion cannot be reconciled with the facts concerning the effect of promoters on the decomposition of molecules of a single type, nor does it agree with the observed effects of promoters on the adsorption of such reactants.

The case of two reactants.

The example discussed above concerned a reaction involving only a single type of molecule, and it is of great interest to consider a more complicated case. This has been done for the interaction of phenol and hydrogen to give benzene and water in contact with molybdenum oxide catalysts.[3] The curves of Fig. 53 show that under these conditions the optimum concentration does not remain quite unaltered with change in the promoter An additional fact of interest is that the concentration required in the present case is quite different from that previously determined in the decomposition of hexane on similar catalysts. It must, however, be remembered that in the latter case the catalyst was in contact with hydrocarbons at 500°, while in the former it has been treated with the system phenol-hydrogen-benzene-water at 450°. The degree of reduction of the original oxide may well be different in the two cases, and this may be the chief contributory factor in the need for an increased promoter concentration.

---

[1] *Ind Eng Chem*, 1926, 18, 1307.

[2] *Naturwiss*, 1926, 14, 103.

[3] Griffith, *Nature*, 1936, 137, 538.

In any case it is evident that the promoter concentration depends on the particular reaction which is taking place, and that different reactants are therefore catalysed by different parts of the catalyst surface or by a distinct oxide of the catalyst element. As to the slight displacement of the optimum on variation of the promoter, more exhaustive tests were not possible in the example under discussion, as extensive compound formation occurred and persisted when attempts were made to employ other elements, but it is not difficult to find an explanation of this phenomenon. The accelerating influence of the promoter will be caused by speeding up the velocity of adsorption and activation of the reactant which normally is more slowly taken up. When this effect

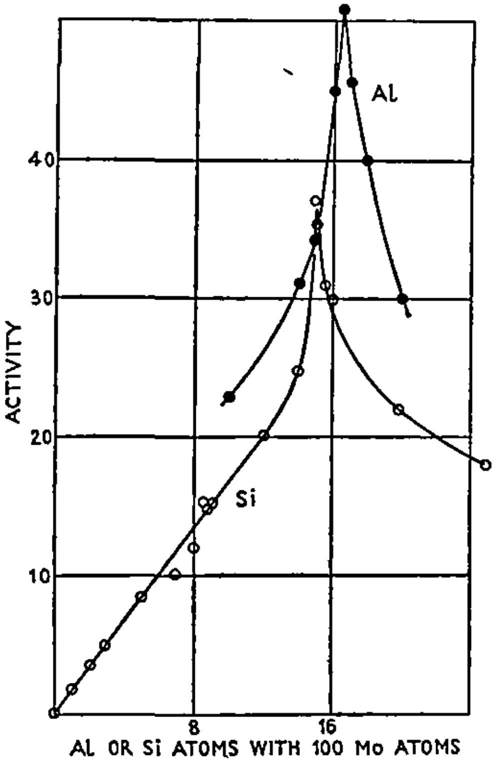


Fig 53. Effect of promoter concentration on activity of molybdenum oxide catalysts for conversion of phenol to benzene at 440°.

is approaching its maximum it may become of the same order as, or even faster than, the velocity of the other reactant. If the effect of the promoters varies in degree, although not in the position of its optimum concentration with respect to each reactant, it is clearly possible for the observed optimum to be slightly displaced on either side of the true optimum by this simultaneous effect. It has already been demonstrated that variation in degree does occur in the case of a single type of molecule. More detailed determinations of adsorption by promoted catalysts would assist in the further elucidation of cases such as this.

The mechanism of promoter action.

H. S. Taylor,[1] as a result of his studies of the effect of thoria as a promoter for nickel catalysts in the reduction of carbon monoxide, suggested that it acted in three different ways: (*a*) by supporting existing active centres, (*b*) by creating additional active surface, and (*c*) by altering the proportions in which the reactants and reaction products were adsorbed. These ideas received further support from the observations of Wyckoff and Crittenden[2] on iron catalysts containing alumina and potassium oxide, in which it was shown that the promoters prevented sintering of the catalyst, but that beyond a critical concentration the activity was lowered by covering of the surface with excess of promoter.

More detailed examination, by means of X-rays, of copper oxide catalysts promoted by magnesia, zinc oxide, chromium oxide, and alumina, and of copper promoted by nickel was carried out by Wagner, Schwab, and Staeger,[3] and it was shown that no change in crystal structure occurred when an increase in catalytic activity was observed. Similar results were obtained by Griffith and Hill[4] after examination of molybdenum oxide-silica mixtures, and Smith and Hawk[5] came to the same conclusions concerning zinc oxide-chromium oxide catalysts which were used for the decomposition of methanol, as the X-ray photographs of the most active mixtures showed no characteristic lines.

[1] *J. Phys. Chem.*, 1925, **29**, 1325.

[2] *J.A.C.S.*, 1925, **47**, 2866.

[3] *Z. phys. Chem.*, 1934, **27** B, 439.

[4] *P.R.S.*, 1935, **148** A, 194.

[5] *J. Phys. Chem.*, 1928, **32**, 415.

In certain cases, however, there is a striking relation between the crystal structure and the catalytic activity, but these must be regarded as due to compound formation and are discussed more fully on p. 68, with particular reference to the synthesis of methanol and ammonia. Natta[1] has also found that bivalent oxides with ionic diameters between 0·6 and 0·9 Å form solid solutions with zinc oxide, distort its crystal lattice, and increase its catalytic activity, while amorphous oxides which form spinels with the zinc oxide lead to a lowering of the activity. It is, therefore, apparent that the presence of a promoter does not generally affect the crystal structure of the catalyst, and that where such changes are detected they are due to some more profound alteration in the composition of the catalyst. Further reference to this point will be found in the discussion of Huttig's results with spinels, on p 123.

Applebey[2] has discussed the means by which oxides, and particularly alumina, promote the activity of iron catalysts used for the synthesis of ammonia. It was found that iron alone was quite an active catalyst but rapidly lost its efficacy, *and that the addition of promoter prevented this decay.* It was also observed that a catalyst prepared from Fe_3O_4 was more active than one obtained from Fe_2O_3, and the use of alumina as promoter is attributed to the isomorphism of Fe_3O_4 and $Fe(AlO_2)_2$; the conditions are therefore most suitable for the existence of barriers of alumina which prevent grain growth or coalescence of the active iron centres. The possibility of the formation of spinels of this type was pointed out by Schenck,[3] with production of substances such as $CaO—Fe_2O_3$ Mittasch and Keunecke, and also Brill,[4] have shown that both α- and γ-Al_2O_3 form mixed crystals with Fe_2O_3, so that when reduction of ferric oxide takes place the alumina is able to inhibit the growth of large iron crystals owing to its very even distribution.

The earlier experiments of Wyckoff and Crittenden[5] on the crystal structure of promoted catalysts for the synthesis of

---

[1] *Giorn. Chem. Ind. Appl*, 1930, **12**, 13.

[2] *P.R S.*, 1930, **127** A, 255.

[3] *Z. anorg Chem.*, 1929, **184**, 1, 39

[4] *Z. Elektrochem*, 1932, **38**, 666, 669.

[5] *J A C.S.*, 1925, **47**, 2866.

ammonia are also significant. They showed that the most useful oxides, to give the promoting effect with iron-oxide catalysts, were of the unreducible type, and would give spinels of the same cubic symmetry as Fe_3O_4, with which they would form solid solutions. They also demonstrated that the size of the crystal lattice was unaffected by the addition of the promoter, but that the growth of iron crystals was greatly diminished by its presence. In the case of cobalt and nickel catalysts used for the reduction of carbon dioxide, Schenck and Wesselkock[1] found that there were clear indications of the existence of mixed crystals in the presence of effective oxides such as magnesia or alumina, and that these led to the production of carbon monoxide under conditions where the pure metals alone had no effect.

With regard to the question of promoter action in general, these authors expressed the opinion that 'it seems highly improbable that a single explanation of promoter action, applicable to all cases, will ever be found'. Unless the definition of promoter action is extremely limited in its scope, this statement may still be accepted. As an example of further complications which may influence the results, mention may be made of experiments of Kobosev, Jerofejev, and Sluchovski[2] on the decomposition of iron nitrides with and without the addition of alumina. The mixture was shown to decompose five or six times as fast as either Fe_2N or Fe_3N, and the surface of the mixture was about eight times that of the nitride; the corrected energies of activation for the decomposition were, however, the same in each case. Natanson,[3] in association with the above experimenters, discovered that the alumina-iron nitride crystallites were of practically the same size as those of Fe_2N alone, and it was concluded that the promoter acted by increasing the surface, suppressing diffusion, and preventing crystallization of the iron.

Simultaneous poisoning and promoting.

The fact that a substance may act as a poison to a catalyst, and yet itself be promoted by that catalyst, is obviously quite

---

[1] *Z. anorg. Chem*, 1929, **184**, 39.

[2] *Z. Elektrochem.*, 1935, **41**, 274.

[3] Ibid, 284.

possible, and is illustrated by the experiments of Neumann[1] with catalysts for the combination of carbon monoxide and oxygen. The general type of activity-promoter concentration curves obtained is shown in Fig. 54 for the case of MnO_2—Ag_2O catalysts; although only points at wide intervals were explored, the curves are of the straightforward promoter type and evidently might give sharp optima on closer investigation.

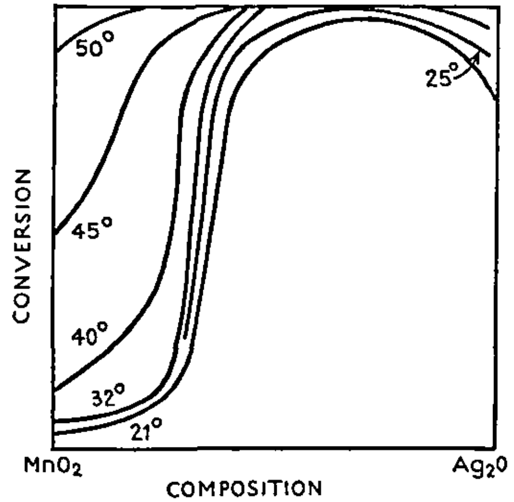


FIG. 54. Results with mixed catalysts in oxidation of carbon monoxide.

In the case of silver manganite-nickel oxide mixtures, however, the former component has a very pronounced poisoning effect on the latter, while the nickel oxide has an equally striking promoter action on the silver compound; this is shown in Fig. 55. In this series of experiments the changes in activity do not coincide with points of possible compound formation, and the effects are attributed to the existence of two-component interfaces in the catalyst. Further reference to this subject will be found in Chapter VI.

Carrier action.

The original purpose in using carriers was to economize in the consumption of an expensive catalyst, such as platinum, by spreading it over a bulky solid material instead of apply-

---

[1] *Z. Elektrochem.*, 1931, 37, 121.

ing it in massive form. A further advantage resulting from the use of a robust carrier was that a catalyst could be obtained in a form which would stand mechanical shock and would not set up back pressure in the reaction vessel by crumbling to a powder. The primary factors in the selection of a carrier were therefore its physical properties and cheapness, which account for the use of pumice, broken brick, charcoal, and similar substances No special attention was paid to the possibility of a specific action of a carrier, and differences of behaviour were attributed to inequalities of distribution of the catalyst itself.

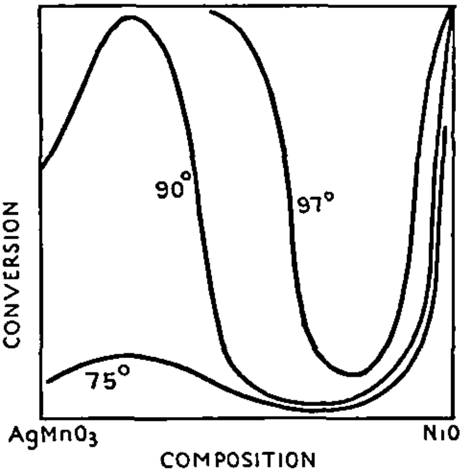


FIG. 55. Poisoning of nickel oxide and promoting effect on silver manganite in mixed catalysts at different temperatures, for oxidation of carbon monoxide

Armstrong[1] used kieselguhr as a carrier for nickel catalysts, and found that it was more effective if another oxide was first deposited on the carrier. He suggested that the inner pores of the kieselguhr were filled up with an inert material, and were thus unable to take up the active catalyst in places where it could not exert its activity. This idea must, for several reasons, be considered unsound, and a clear distinction must be drawn between cases of carrier action proper and mixed catalysts.

---

[1] *P.R.S.*, 1923, **103A**, 594.

Experiments by Sabalitschka and Moses[1] indicated that complications might arise on account of some specific effect of the carrier. They studied the hydrogenation of maleic and fumaric acids in the presence of palladium deposited on a range of carriers such as charcoal, kieselguhr, and barium sulphate, and found that the activity depended on the carrier as well as on the manner in which the deposition had been carried out. They considered that the carrier facilitated close contact between the organic compound and the hydrogen which was adsorbed by the palladium, and that the carrier had an additional function in preventing the coagulation of the finely divided metal.

In further experiments by Sabalitschka and Zimmermann[2] an attempt was made to follow the effect of barium sulphate and charcoal more closely when they were used as carriers for palladium in the hydrogenation of fumaric acid. It was observed that a lowering of catalytic activity was sometimes produced which depended on the amount of carrier present, but no simple explanation of this behaviour could be found.

For the purpose of the present discussion it will be assumed that the carrier itself is a substance with negligible catalytic activity for the particular reaction in question. Some data of Zelinskii and Balandin[3] are of considerable interest in this connexion, as they have shown that the carrier may be entirely inert with respect to the mechanism of the reaction. Using platinum as a catalyst for the dehydrogenation of a series of organic compounds, they found that the energy of activation for the decomposition was independent of the particular carrier on which the metal was dispersed, and of the relative activity of the catalysts Results for the dehydrogenation of dekalin and of cyclohexane are given in Table 12.

Some results described by Baly,[4] on the other hand, suggest that when a solid is supported on a carrier its condition may undergo considerable changes which influence its catalytic activity. Aluminium hydroxide was deposited on kiesel-

---

[1] *Ber.*, 1927, **60** B, 786.

[2] Ibid , 1930, **63** B, 375.

[3] *Z. phys Chem.*, 1927, **126**, 267.

[4] *J S.C.I.*, 1935, **55**, 9 T, *Nature*, 1935, **136**, 28.

guhr by precipitation from dilute solutions of aluminium nitrate, and the dried product was then suspended in aqueous acetic acid while measurements of its surface potential were made. It was found that the value of the potential increased in a linear manner with the amount of alumina deposited, up to a maximum beyond which it fell to a steady figure which was the same as that given by unsupported alumina. The position of the maximum corresponded approximately to a unimolecular layer of aluminium hydroxide, and it was evident that the substrate had somewhat modified the properties of the deposit although no study had been made of corresponding changes in catalytic activity. This method has possibilities in the direction of determining the saturation point of a rigid carrier for any particular deposit or the concentration of a catalyst which may safely be regarded as giving effects free from the carrier's influence, but little indication can be given as to the modification which the carrier may cause in the activity of the catalyst.

TABLE 12

Energy relations in dehydrogenation of hydrocarbons

Substance	*Catalyst*	*Energy of activation K.-cals.*
Dekalin	Pt-charcoal	18 89
,,	Pt-asbestos	18 99
Cyclo-hexane	Pt-charcoal	18 04
,,	Pt-asbestos	18 04

Further experiments which have been carried out with substances of this type[1] show that three distinct effects may be noted, as already outlined in the opening paragraphs of this chapter. These will be illustrated and discussed in turn.

1. *Addition of carrier produces an increased catalytic effect.*—As an example of this case, the use of metallic copper for the dehydrogenation of dekalin may be considered. The catalyst was prepared by reduction of pure copper oxide to which varying proportions of magnesium oxide were added, the latter functioning as the carrier. The catalyst prepared by

---

[1] Griffith, unpublished data.

the reduction of copper oxide alone had an initial activity which completely vanished after a few hours, and at the end of this time it was found to be in the form of hard metallic lumps. The addition of a small amount of magnesium oxide, however, prevented this loss of activity, and a point *X* on the curve of Fig. 56 was obtained. On further addition of carrier to the catalyst the activity remained unaltered over a wide range of concentration until it began to fall again at *Y*. It then followed a straight line through *Z* to the figure representing the activity of the carrier alone. These results are all presented on a volume basis, and not on that of the absolute weight of copper which is in the mixture; they would obviously be different in form if expressed in that manner.

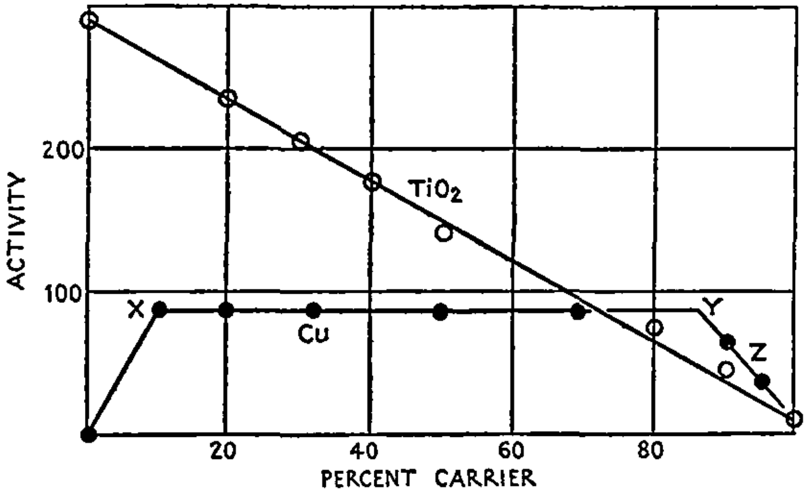


FIG. 56. Carrier action with titanium oxide and with copper catalysts, for dehydrogenation of dekalin at 500°, and added magnesium oxide.

X, prevention of sintering complete.
Y, dilution begins.
Z, oxide not reduced to metal.

At the same time it was noted that the reduction of copper oxide to metallic copper had no longer taken place when the point *Y* was reached. The results show that an inert carrier may have a very material effect in preventing the sintering of an active metal surface, which may otherwise occur to such an extent that the whole mass is fused into inert lumps.

A point is, however, reached when excess of the carrier is added, and the conversion of the inactive metal oxide into the active metal is prevented by the excess of carrier. It is, however, a matter for further comment that no immediate dilution effect should set in once sufficient carrier has been added to prevent the sintering of the pure copper.

2. *The addition of carrier produces a delayed dilution effect.*—The observation recorded above for the case of copper is not an isolated example of what may be termed delayed dilution, but simpler examples are known which are not complicated by the preliminary enhancement shown with the foregoing type. The fact that inert carriers, such as china-clay, could be added to molybdenum oxide catalysts for use in high-pressure hydrogenation of tar oils was recorded by Hollings, Griffith, and Bruce,[1] and suggested that the explanation for this occurrence might be found in the very large size of the molecules present in the tar oil. Further experiments with hydrocarbons of different molecular dimensions have now shown that this is, in fact, the case.

Chromium oxide was chosen as the catalyst for effecting the dehydrogenation of dekalin, decane, cyclohexane, and hexane, under standardized conditions of temperature and pressure. The experiments were in every case continued until a steady value for the activity had been obtained for a period of some hours, and no importance was attached to the initial results which were observed.

In Fig. 57 are shown the results of these experiments, and it is immediately evident that a much higher proportion of carrier can be added in the case of the large dekalin molecule than is tolerated when decane is the reactant, while with hexane an immediate dilution effect sets in. It must therefore be concluded that the hexane molecule can reach all the active parts of the pure catalyst, but that neither decane nor dekalin can do so, and with the latter particularly the steric effect is very pronounced. The place of cyclohexane in this series of experiments is anomalous, as it does not lead to the production, in the reaction vessel, of the same oxide of chromium as the other three hydrocarbons give. Although

---

[1] *P.R.S.*, 1935, **148** A, 186.

the activity of this oxide in its pure state is relatively high, it suffers extremely rapid lowering on the addition of carrier. On passing cyclohexane over a catalyst which had previously been in contact with dekalin, only very slight decomposition could be observed, a fact which is in accord with the data concerning cyclohexane already presented for molybdenum catalysts.

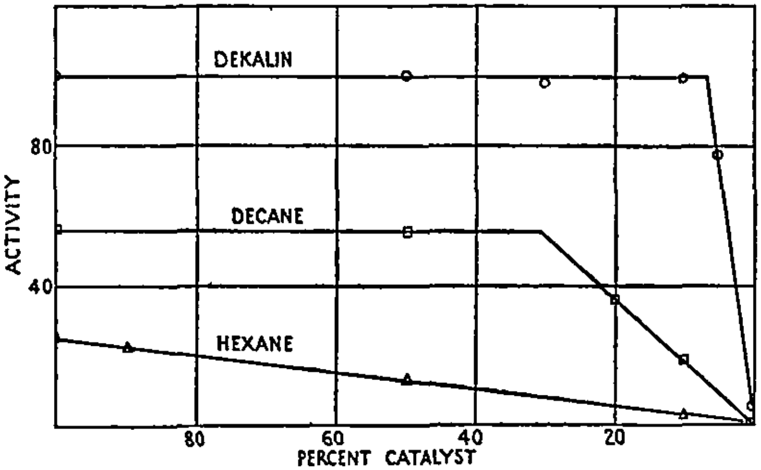


FIG. 57. Effect of carrier concentration on chromium oxide catalysts.

The observations of Balandin[1] on the relation between catalyst activity and the energy of activation for the reaction appear to have some significance in connexion with this phenomenon of delayed dilution. Although the determinations are open to objection on the grounds that data for heats of adsorption are not available, so that the observed activation energies cannot be corrected to the true value, there was apparently no need for the introduction of a term involving the number of active centres in the catalyst into the equation, although platinum, palladium, and nickel were used for a wide variety of dehydrogenation reactions. Such a result would be arrived at if the number of active centres was always greater than the number of reacting molecules which could be packed on the surface.

The question of molecular dimensions may evidently

---

[1] *Z. phys. Chem.*, 1932, 19 B, 451.

become even more important in dealing with such materials as hydrocarbons contained in the higher boiling fractions of coal tar. This is well illustrated by some results obtained at the Fuel Research Station during the hydrogenation of low-temperature tar. The whole tar, or a distillate from this, was treated at 200 atmospheres pressure and 480° under standardized conditions of through-put in a continuous hydrogenation plant, and the amount of ammonium molybdate added to an alumina-gel carrier, for the preparation of the catalyst, was varied between 5 and 25 per cent.[1] In Table 13 the yields of the spirit fraction in the different products are tabulated, this being a convenient measure of catalyst activity. It is evident that, in the case of treatment of the whole tar, the maximum effect is already obtained with a catalyst containing only about 10 per cent. of molybdate, but with the tar oil about 15 per cent. is required. These observations are in complete agreement with the foregoing discussion, as the average molecular weight will be appreciably larger with the whole tar than with the distilled tar oil.

TABLE 13

Hydrogenation of coal-tar with molybdenum oxide catalysts

Per cent ammonium molybdate	*Per cent. spirit from tar*	*Per cent. spirit from tar oil*
5	27·0	53·4
10	33·1	58·2
15	34·1	63·1
20	35·7	65·2
25	33·9	62·7

3. *A straight dilution effect takes place.*—There is not always this delayed dilution even with the largest molecules, and the case of titanium oxide (Fig. 56) shows that a catalyst with a high activity may be diluted instantly on addition of carrier. That this dilution is not a case of poisoning is shown by the fact that it occurs similarly with carriers other than magnesia, and that poisoning of titanium oxide by alkali only requires very small quantities of the latter to give complete inactivity. The explanation must lie in the fact that some

---

[1] *F.R.B. Annual Report*, 1934, 80.

catalysts contain very large numbers of active centres while others have relatively few; similar observations will be found in connexion with catalyst poisons.

Carrier action and promoted catalysts.

The ideas concerning carrier action which are outlined above suggested that the behaviour of promoted catalysts on the addition of a carrier might give valuable information as to the function of a promoter. If the latter increased the number of active centres it would be expected that the dilution effect, on addition of an inert carrier, would occur at a smaller catalyst concentration with the promoted catalyst than it did with the one-component catalyst. This point was investigated with chromium oxide-silica catalysts and magnesia as a carrier, using the dehydrogenation of dekalin as the reaction.

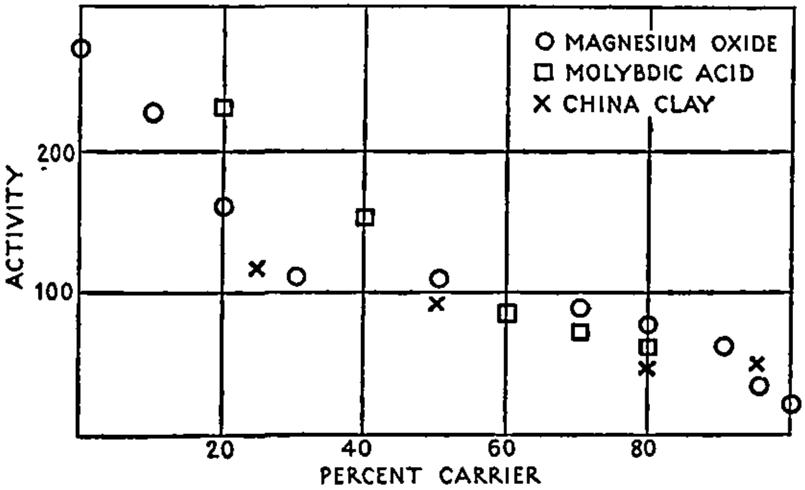


FIG 58 Effect of dilution on a promoted chromium catalyst, used in the dehydrogenation of dekalin.

The addition of silica to chromium oxide gave a promoter curve of the usual form, so that this may be taken as a typical example. When the promoted catalyst was mixed with the carrier, however, an immediate dilution took place as shown in Fig. 58. This occurred equally with other carriers such as china-clay or molybdic acid, and it must be concluded that the addition of the promoter has not increased the number of active centres but has formed a surface of an entirely different type.

Dual catalysts.

Reliable examples of what may be termed 'dual catalysts' are very rare. The conditions to be fulfilled are that both the components alone are inactive, but that together they provide an efficient catalyst, without the occurrence of compound formation. Merck and Wedekind[1] investigated a series of cobalt oxide catalysts for the oxidation of carbon monoxide, and found that neither pure CoO(OH) nor Co_3O_4 alone was active, but that together they were very effective. On the basis of measurements of magnetic susceptibility, however, there was some evidence for the existence of a compound which provided this activity.

The action of promoters on molybdenum oxide, used as a catalyst for the conversion of phenol to benzene, has already been described, and is an example where the single component has no permanent activity, but this falls rather outside the intention of the above definition. In the case of copper oxide-magnesia mixtures also discussed, another explanation of the phenomenon has been found. Again, in the example of molybdenum oxide on supports such as bauxite or charcoal,[2] where the oxide alone has no permanent activity, there is no evidence that the two reactants, i.e. phenol and hydrogen, are adsorbed separately by the two components in the effective mixtures.

It must be concluded that experimental evidence on this subject is insufficient, but that there is no reason for supposing that such circumstances will never be proved to exist, where different types of molecule are held on distinct parts of a catalyst.

---

[1] *Z. anorg. Chem.*, 1930, **186**, 49; **192**, 113.

[2] *F.R.B. Annual Report*, 1933, 89.

CHAPTER IV

POISONING AND RETARDATION

A FALLING off in activity of catalysts during use has been observed from the days of the earliest studies on the subject, and has led to the recognition of catalyst poisons and of retardation. Although other causes of a decrease in activity can arise, the study of poisons is of such great technical and theoretical importance that its separate treatment is justified.

Poisoning may occur either from the presence of impurities in the catalyst during its preparation, or from substances in the reactants which are being treated, and in both cases the effects may be permanent or transitory. The latter class of poisoning has been long recognized and will be discussed first.

Poisoning from reactants.

The general cause of poisoning from the reactants is the presence of small amounts of impurities in these substances, and two typical examples will serve to illustrate the manner in which this may occur. In the synthesis of ammonia the iron catalyst is rapidly poisoned by the presence of small concentrations of hydrogen sulphide or of water vapour. In the former case the effect is permanent and irreversible, reactivation of the catalyst only being achieved by ignition and fresh reduction with hydrogen, and is due to the stability of iron sulphide under the conditions of experiment. The iron sulphide has no catalytic activity for the synthesis of ammonia.

The case of water vapour, however, is reversible as the effects are eliminated by thorough drying of the gases; the inactive iron oxide which is formed in this case is only stable in the presence of a definite concentration of water vapour. Ussatschev and others[1] have also shown that oxides of carbon, sulphur dioxide, nitrous and nitric oxides, and water behave similarly in lowering the formation of ammonia from nitrogen and hydrogen. The immediate effect of the addition to the reacting gases is a temporary increase in the ammonia concentration of the reaction products owing to displacement

---

[1] *Z. Elektrochem.*, 1934, 40, 647.

from the catalyst surface. If, on the other hand, uranium nitride is used as the catalyst for the synthesis of ammonia, it is permanently poisoned by the presence of water vapour, because it is converted into a stable oxide which has no catalytic activity.

A closer study of the behaviour of iron catalysts was made by Almquist and Black[1] in which controlled amounts of oxygen were added to the inlet gas, and results such as those of Fig. 59 were obtained. During the period of rapid drop in activity water was detected in the outlet gases, but always in less amount than was equivalent to the added oxygen, showing that iron oxide was formed. When oxygen-free gas was supplied to the catalyst, this oxygen was completely removed in the form of water. With promoted iron catalysts a larger amount of oxygen was retained by the surface than with pure iron, so that the same active centres appear to be responsible for combination with oxygen as are concerned in the catalytic reaction, and by determination of the relative

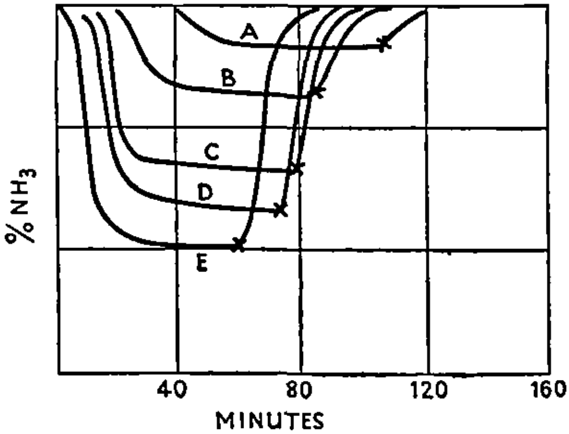


FIG. 59. Effect of oxygen on promoted iron catalyst for synthesis of ammonia.

A with 0·02% oxygen.
B „ 0·04 „
C „ 0·08 „
D „ 0·16 „
E „ 0·24 „

Oxygen cut off at points marked X.

---

[1] *J.A.C.S.*, 1926, 48, 2814.

amounts of oxygen combined with promoted and unpromoted catalysts it was concluded that the former contained one active iron atom in about two hundred, while the latter only had one in about two thousand. Emmett and Brunauer[1] extended this series of experiments to high pressures, and the effect of addition and removal of water on the activity of an iron-alumina-potassium oxide catalyst is shown in Fig. 60.

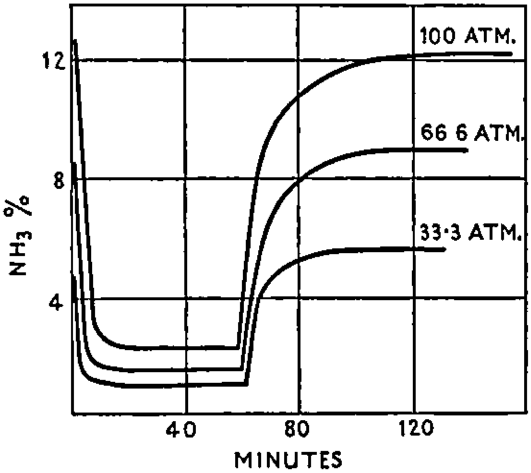


FIG. 60. Effect of 0 32% H_2O on iron-alumina-potassium oxide catalyst. Water cut off after 1 hour.

The initial activity was practically regained when the water was eliminated from the system, but a slight total decrease in its value resulted after many repetitions of the poisoning.

The promoted catalyst again took up much more oxygen from the water than was the case with pure iron; the amount retained at 450° was approximately proportional to $\sqrt{P_{H_2O}}/\sqrt{P_{H_2}}$, which suggested that it was held in the form of a compound and not as adsorbed water. The calculated ratio of active to inactive iron atoms under the high-pressure conditions was found to be in good agreement with the results obtained by Almquist and Black.

A similar effect has been noted by Roberti[2] with nickel catalysts used for the conversion of benzene to cyclohexane. The extent of poisoning by thiophene depended on its partial

---

[1] Ibid., 1930, **52**, 2682.

[2] *Gazzetta.*, 1933, **63**, 46.

pressure in the gaseous phase, and not on the total quantity of the sulphur compound which was passed over the catalyst.

Specific nature of poisons.

The specific nature of the effect of poisons was emphasized by the data of Hoover and Rideal[1] concerning the decomposition of alcohol in contact with thorium oxide, which could take place either by dehydration and ethylene production, or by dehydrogenation with the formation of aldehyde. The former reaction was more retarded by the presence of aldehyde in the system than was the case with the alternative reaction. Small amounts of chloroform poisoned the dehydrogenation reaction but accelerated the dehydration, while larger concentrations of chloroform poisoned both processes. This selective poisoning effect indicates that different parts of the catalyst are concerned with the alternative reactions, a conclusion which has been arrived at from other independent pieces of evidence.

Considerable difficulty has been experienced in reconciling the evidence afforded by adsorption measurements on poisoned catalysts with the foregoing assumptions. It would be expected that adsorption of the reactants would be greatly inhibited by the presence of a poison. Pease and Stewart[2] investigated this point with a copper hydrogenation catalyst, and found that the addition of 0·03 c.c. of carbon monoxide to material which had an adsorptive capacity of 1 c.c. of hydrogen (at 1 mm. pressure) lowered the activity by over 90 per cent. This indicates that catalytic activity may be greatly reduced without saturation of the surface of the adsorbent, but it must be emphasized that the measurements were not made at temperatures where activated adsorption is now known to take place. From the discussion on adsorption in a previous chapter it will be seen that lack of agreement between poisoning and adsorption data for low temperatures is of no significance and that this point demands much further attention. Similar criticisms apply to the measurements of Griffin[3] on poisoned copper catalysts at 0°

[1] *J.A.C S*, 1927, 49, 104.

[2] Ibid, 1925, 47, 1235.

[3] Ibid., 1935, 57, 1206.

in which increased adsorption of hydrogen was even observed in some cases when carbon monoxide was also present.

The evidence of Farkas, Farkas, and Rideal[1] for the case of para-hydrogen conversion inhibited by ethylene is much clearer, and gives an excellent picture of reversible poisoning due to selective adsorption. An activated platinum wire was prepared by alternate oxidation and reduction, and was used as a catalyst for the production of ortho-hydrogen and simultaneously for hydrogenation of ethylene. In Fig. 61 are shown velocity curves for the conversion of para-hydrogen alone, with the addition of ethane and with addition of ethylene. It is evident that the effect of the presence of ethane is practically negligible, but that ethylene almost completely inhibits the change; as the hydrocarbon is converted to ethane, however, a point is reached at which the active surface is no longer covered and adsorption of hydrogen can take place; the change to ortho-hydrogen then proceeds at the normal rate.

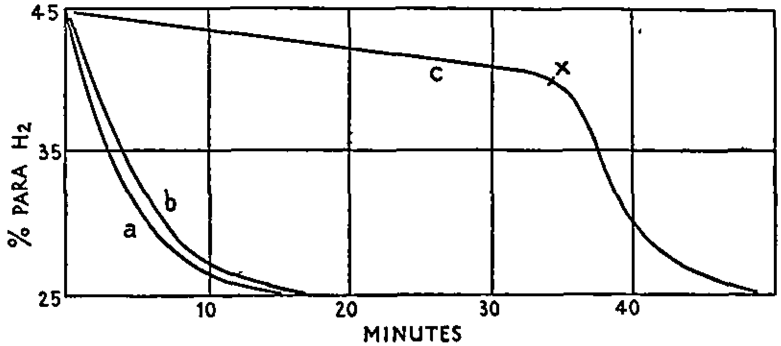


FIG. 61. Conversion of para-hydrogen in presence of hydrocarbons.
A, 25 mm. hydrogen
B, „ „ +17 mm ethane.
C, 23 mm. „ +19 mm. ethylene.

At point X, ethylene pressure had fallen to about 2 mm During first 30 mins. curve *C* was exactly linear, i.e. the reaction is of zero order.

Typical of a slightly different class of poisoning is the behaviour of vanadium catalysts for oxidation of sulphur dioxide,[2] in which the rate of reaction is directly proportional

---

[1] *P R S.*, 1934, **146 A**, 630.

[2] Adadurov, *Trans. VI. Mendeleev Cong. Theor. Appl. Chem.*, 1935, **2**, 154, Boreskov, ibid., 159.

to the concentration of dioxide and inversely proportional to the square root of the concentration of trioxide. A sudden fall in activity is noted if the temperature is dropped to 400° and is due to the formation of a vanadium sulphoxide, if the temperature is raised slightly above this point the inactive compound is decomposed. At the same time the catalyst is susceptible to poisoning by arsenic, but in this case the effect is permanent as the compound which is formed is stable and inactive.

Poisoning mechanism.

Although it was appreciated at an early stage in the development of the theories of contact catalysis that very small concentrations of poisons had a marked effect on the surface, considerable confusion has arisen from a publication by Vavon and Husson[1] concerning progressive poisoning. They found that a platinum catalyst could be poisoned by the addition of a small quantity of carbon disulphide as far as its action in the hydrogenation of propyl ketone was concerned, but that the catalyst was still active for the hydrogenation of piperonal. The addition of more carbon disulphide in turn suppressed the latter reaction, but the catalyst remained effective for hydrogenation of nitrobenzene. Some later investigations of Maxted and his co-workers[2] have thrown some doubt on the significance of these observations and have made the whole position very much clearer.

Maxted found that, in the poisoning of platinum catalysts by means of lead, mercury, or arsenic, as in the case of the oxidation of sulphur dioxide, the activity of the catalyst was a linear function of the concentration of the poison in the range of fairly small amounts of the latter. Fig. 62 illustrates this point for the case of sulphur dioxide in contact with platinum poisoned by arsenic. This shows that the effect of the first additions of the poison was considerably larger than that of the final amounts, but that only two types of active centre appeared to be involved and that the complete suppression of activity was seldom attained or required relatively

---

[1] *Compt. Rend*, 1922, **175**, 277.

[2] *J.C S*, 1922, **121**, 1760, 1925, **127**, 73; 1928, 1600, 1934, 26, 672.

very large amounts of poison. The activity of any particular poison may be expressed as a poisoning coefficient α which is given by the relation

$$K_c = K_0 (1-\alpha c)$$

where K_c is the reaction velocity constant in presence of a concentration c of poison, and K_0 is the constant in the absence of poison

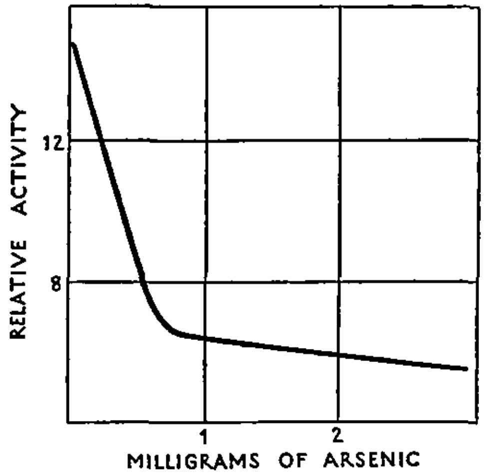


FIG 62. Effect of poison on 0·35 gr. platinum

When this method of comparison was applied to the case of platinum catalysts used for hydrogenation of nitrobenzene, acetophenone, benzene, and oleic acid in the presence of mercury as a poison, or of acetophenone and benzene with carbon disulphide as a poison, the poisoning coefficients were found to be independent of the material undergoing hydrogenation. In its early stages, therefore, poisoning appears to be equally effective on all parts of the active surface; further reference will be made to this point later in Chapter VI in connexion with theories of active centres in the catalyst.

Similar poisoning curves were obtained by Maxted and Lewis[1] in the case of platinum-black catalysts used for the decomposition of hydrogen peroxide and poisoned by mercury ions. When the unimolecular reaction constant for the decomposition was plotted against the concentration of poison, a

---

[1] *J.C S.*, 1933, 502.

curve similar to that of Fig. 62 was obtained, and it is suggested that the initial linear portion of the line is due to that part of the adsorption isotherm for mercury on platinum which itself is linear. After a time, however, an increase in the concentration of mercury ions in the solution can no longer give a corresponding increase on the surface of the catalyst. The value of the apparent energy of activation for the reaction was also found to be uniform at all stages of the poisoning.

Reversal of poisoning.

Russell and Ghering[1] investigated the poisoning of copper catalysts, used for ethylene hydrogenation, by means of oxygen and obtained linear effects similar to those described by Maxted. But on reactivation of a poisoned catalyst by controlled reduction, curves of an entirely different character were obtained which indicated greater catalytic activity of those parts of the surface which had the greatest affinity for oxygen. Although it was found that the oxygen absorption was non-selective, as the gas was completely consumed by the first layer of copper, it must be remembered that alternate oxidation and reduction of a metal-metal oxide system frequently leads to the production of a catalyst with enhanced activity, and the fully reduced product in the present case had, in fact, a greater efficiency than the parent material.

Poisoning by admixture with the catalyst.

The risk of poisoning not only arises from impurities which are present in the reactants but may arise from the treatment which the catalyst has received prior to use; changes due to physical causes must not be included under this heading, and are discussed more fully in the following chapter.

It has been indicated that compound formation often leads to a two-component catalyst having a higher activity than that consisting of a single component. It is equally possible, of course, for the compound to have a much lower activity or even to be entirely without effect; this may be called

---

[1] *J.A.C.S.*, 1935, 57, 2544.

poisoning by compound formation, and will arise when the particular compound—such as a sodium salt of a strongly acidic oxide, for example—is very stable and has a distinct crystal structure of its own. The stability may lead to failure of the compound to undergo reduction to an active state under conditions where the single component would have been changed.

Poisoning also appears to be possible by the addition of small quantities of a second substance under conditions where compound formation is excluded; for instance, the need for washing precipitated catalysts quite free from soluble salts has often been noted. A similar example is presented by the poisoning of titanium oxide catalysts, used for the dehydrogenation of hydrocarbons, by the addition of small amounts of caustic soda or of calcium chloride (unpublished data). This was found to be due to the fact that reduction of the inactive brown oxide to the active black oxide did not occur when free alkali was present. Although little information is yet available in this direction it is probable that such facts will account for most of the observations of this kind.

Retardation.

The term retardation is applied to the suppression of catalyst activity by means of either reactants or reaction products, whose presence is not due to impurities and which cannot generally be prevented from playing their part on the catalyst surface. The theoretical significance of the phenomena of retardation is of very great interest and is dealt with fully in Chapter VII, but the more practical consideration of the matter has such a close relation to poisoning that it demands discussion of a few typical examples.

Apart from the experiments of Hinshelwood and Langmuir, the following are interesting cases: Zelinskii[1] found that the gradual loss of activity of catalysts used in the decomposition of organic compounds was due to the deposition of sooty material on the surface, and that the initial activity could often be restored by oxidation at relatively very low

---

[1] *Ber.*, 1926, 59, 156.

temperatures, thus indicating that the deposit is very closely associated with the active parts of the surface. In the investigation of catalysts by dynamic methods cases of retardation are very rarely observed, but Constable[1] found that the velocity of the decomposition of alcohol by a copper catalyst increased with the rate of flow, in the range of high times of contact. H. A. Taylor and Pickett[2] similarly found that an initial increase in decomposition of hydrogen sulphide by means of a platinum filament took place when the rate of gas flow was raised. A third example has been detected in the interaction of carbon disulphide and sulphur dioxide with a titanium sulphide catalyst,[3] where the degree of conversion varied with the rate of throughput in the manner shown by Fig. 63. These three cases must be explained on the grounds of retardation due to the adsorption of one or more of the reaction products.

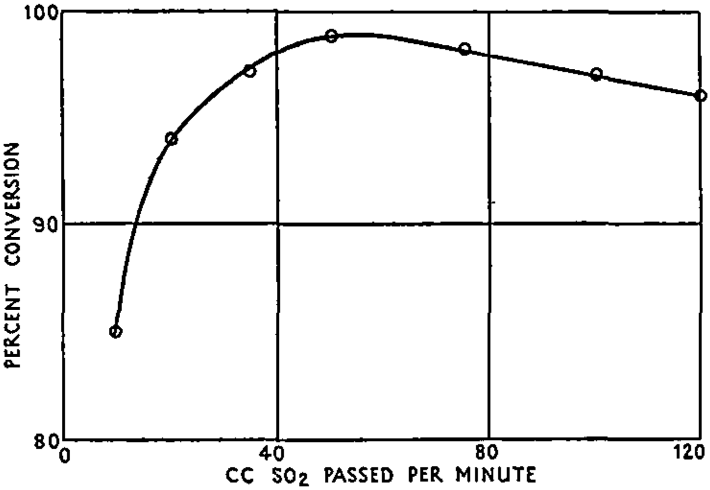


Fig. 63. Effect of rate of passage, of equimolecular mixture of sulphur dioxide and carbon disulphide, over titanium sulphide catalyst at 450°, showing retardation at low rates.

In the decomposition of ammonia retardation is caused by hydrogen when the catalyst is iron,[4] but by both nitrogen

---

[1] *Proc. Camb Phil. Soc*, 1927, **23**, 593.

[2] *J. Phys. Chem*, 1927, **31**, 1212.

[3] Crawley and Griffith, unpublished data

[4] Kunsman, *J.A C S.*, 1929, **51**, 688.

and hydrogen when osmium is used.[1] The latter case is illustrated in Fig. 64, where it can be seen that the effect is very pronounced in the case of hydrogen and, in the initial stages, is almost directly proportional to the concentration of the retarding gas which is added. The highly specific effects observed with the different catalysts and different retarding substances are characteristic of such phenomena. At the same time the precise form of the catalyst does not appear to be significant, as it has been shown by Steacie and McCubbin[2] that the decomposition of nitrous oxide on spongy platinum agrees with that on a platinum filament in being retarded by oxygen. These observers also showed that oxygen formed in the decomposition had a greater retarding effect than if it were added from an outside source, probably owing to adsorption taking place, in the first case, when the oxygen was in an atomic state.

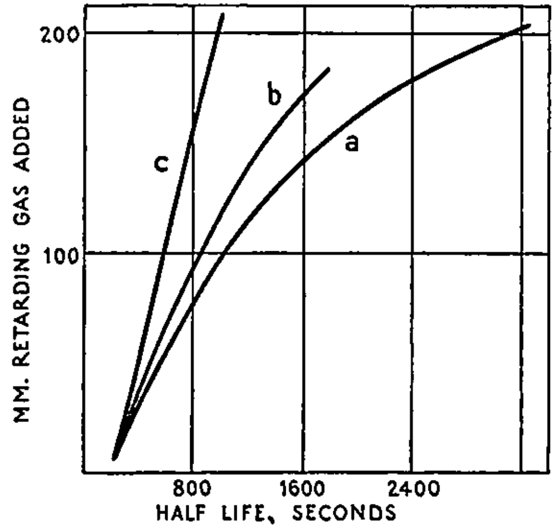


FIG. 64 Decomposition of ammonia on Osmium at 340°.

A, added hydrogen.
B, „ products from decomposition.
C, „ nitrogen.

---

[1] Arnold and Burk, *J.A C S.*, 1932, 54, 23.

[2] *J. Chem. Phys.*, 1934, 2, 585.

The results of Chapman and Gregory[1] on the behaviour of palladium catalysts for the combustion of hydrogen suggested that selective adsorption of the retarding gas—in this case hydrogen—may take place to such an extent that no reaction occurs even when the mixture is admitted to a cleaned catalyst surface. Owing to the heat treatment which the palladium had undergone, however, it seems more likely that some other explanation would fit the facts, and the experiments of Finch and Bradford, which are described on p. 125, should be considered in this connexion.

Reactivation of poisoned catalyst.

The fact that temporary poisoning can be overcome by removal of the offending compound from the reactants has already been made clear, but when the poisoning is permanent, or when retardation is caused by some reaction product of very low vapour pressure, more drastic measures are necessary in order to restore the activity of the catalyst. An illustration of regeneration by destruction of the retarding substance can be found in the case of vanadium oxide used for the conversion of phenol to benzene. The effectiveness of the material gradually falls, as shown in Fig. 7, on account of the deposition of pitch-like compounds which are formed by side reactions giving highly polymerized organic bodies. When the reaction mixture is cut off from the catalyst and a stream of air is supplied instead, as at point X in the curve of Fig. 7, the undesirable products are removed from the surface and the initial activity of the catalyst is restored. When fresh supplies of reactants are brought into contact with it again, the decrease in activity again takes place in precisely the same way.

The catalysts of Fischer,[2] consisting of nickel with promoters such as manganese and aluminium oxides, which are used for the synthesis of hydrocarbons by the interaction of carbon monoxide and hydrogen, are particularly interesting as they suffer from poisoning of both kinds. The life of the catalyst is greatly shortened by the presence of sulphur compounds in the reaction gases, the formation of sulphides giving

---

[1] *P.R.S*, 1934, 147A, 68.

[2] *Brennstoff-Chemie*, 1935, 16, 1.

rise to permanent poisoning. When the reactants are quite free from all sulphur, however, there is a gradual loss of activity, so that the temperature of the catalyst has to be raised slowly in order to produce the same degree of conversion; this retardation has been shown to be due to the deposition of waxy hydrocarbons[1] which may be removed from the catalyst by extraction with a suitable solvent

The process of elimination of carbon disulphide from coal gas, developed by the South Metropolitan Gas Co., provides another example of the recovery of activity after temporary poisoning. Evans[2] reported that the nickel catalyst used in the hydrogenation reaction, which led to the formation of hydrogen sulphide, lost its efficiency during four or five weeks' operation, and then needed treatment for one week with a carefully controlled air-stream at a gradually rising temperature in order to remove the carbon deposit. The catalyst was then as good as before and showed no permanent loss of activity after two years' use with periodic regeneration.

In more extreme cases of retardation it may be necessary to clean the surface under such severe conditions that sintering occurs simultaneously; this will call for complete chemical attack of the compound and reprecipitation of a suitable starting material before an active catalyst can be reproduced. Such roundabout means of regeneration are very laborious, and all possible steps would be taken in practice to avoid such a necessity.

[1] *Brennstoff-Chemie*, 1932, **13**, 61.

[2] *J.S C.I*, 1915, **34**, 9.

CHAPTER V

EXAMINATION OF THE CATALYST SURFACE

MANY attempts have been made to explain the behaviour of catalysts, or the phenomena of adsorption, on the basis of chemical and physical changes which can be recognized in the contact material. These may be classified broadly under the following headings:

1. The surface area of the catalyst.
2. Changes in density and other physical properties, particularly with reference to two-component catalysts.
3. Chemical changes in the catalyst compound which take place before or during use.
4. The crystal structure of active substances as revealed by X-ray examination.
5. The surface structure as indicated by microscopic or by electron diffraction methods.
6. Various other factors affecting activity.
7. Changes which occur during ageing or loss of catalytic activity.

These points will be discussed separately in some detail.

1. *The surface area of catalysts.*

Several investigations have been carried out to determine whether any simple relation exists between the surface of a catalyst and its activity, such experiments being prompted by the realization that a finely divided metal was more active than one in the massive state. Schmitt[1] sought to measure the surface of nickel catalysts by comparing their rate of dissolution in hydrochloric acid, but such methods are open to serious objection owing to the number of other factors which may affect the results. Constable adopted a different line of attack in a series of papers dealing with copper and nickel surfaces,[2] and followed the change in total surface as well as the disappearance of active centres by measurement of elec-

---

[1] *Z. Phys Chem.*, 1925, **118**, 193.

[2] *J.C.S.*, 1927, 1578; *P.R.S.*, 1928, **119** A, 197, 202.

trical conductivity or by the determination of the colour of thin films during sintering of the catalyst. Various times of heating at 440° were used to give progressive decrease in the activity towards the dehydrogenation of alcohol, with the results shown in Table 14. The surface is thus reduced to one-third of its original value, while the activity falls to about one-seventh, but on the basis of unit area shown in the last line it appears that the decrease due to the lower activity of the active centres is not so pronounced as that caused by the diminution of area alone. The conclusions of Constable have, however, been criticized by Rideal,[1] as his arguments are based on the assumptions that the films used were of uniform thickness, and this does not appear to be probable.

TABLE 14

Effect of sintering on catalyst activity

Minutes sintering . .	0	10	50	100	200
Fractional surface area .	1·0	0·72	0·468	0·32	0·33
Rate of dehydrogenation .	3·21	1·71	0·47	0·43	0·43
Reaction velocity per unit area	1·0	0·74	0·31	0·42	0·40

Bowden and Rideal[2] adopted an alternative method for the determination of surface area, and measured the change in electrode potential at the surface of a metallic cathode during removal and deposition of very small quantities of hydrogen by electrolytic action. It was found that the electrode potential was a linear function of the surface concentration of hydrogen, and was independent of the composition of the underlying metal. Any differences which were observed were therefore caused by changes in the true area of the metal, so that the measurements could be applied to the evaluation of the latter. The catalytic activity of the same metal surfaces for the discharge of hydrogen ions from dilute sulphuric acid was then determined, the rate of hydrogen evolution divided by the true area of the cathode being a measure of the specific effect of the catalyst.

As an example of the results obtained the data for nickel are presented in Table 15.

[1] *T. Farad. Soc.*, 1932, **28**, 139.

[2] *P.R.S.*, 1928, **120** A, 59, 80.

TABLE 15

Area and activity of nickel surfaces

Treatment	*Accessible area per apparent cm*^{2}	*Hydrogen evolved per true cm*^{2}*, relative*
Polished, new	13·3	760
„ old	9·7	350
*Activated, new	46·0	240
„ old	29·0	290
Annealed, new	10·8	330
„ old	7·7	230
Electroplated, new	12·0	180
„ old	9·5	140
Rolled, new	5·8	610
„ old	3·5	400

* This was prepared by alternate oxidation and reduction of the metal.

It can be seen that very large variations in the effective area are produced by alternative means of preparation, but that the fluctuations in specific activity are of a smaller order. It is also of interest to note that the areas determined by this method are greater than those arrived at by Constable's technique.

Schwab and his fellow investigators[1] have applied different methods to the determination of the surface area of catalysts. Nickel produced by different methods was used for the reduction of ethyl cinnamate, and the initial rate of dissolution of the metal in acid was compared with that of a polished nickel sheet. It was found that the catalytic activity increased more rapidly than the surface area, indicating that an increase in the specific activity of the effective area had taken place.

In the case of catalysts composed of one or more of the oxides of copper, zinc, and magnesium together with metallic nickel, an increase in catalytic activity was not found to correspond with a greater surface area when the latter was determined by the adsorption of dyes such as methylene blue or β-naphthol orange. Hampel,[2] on the other hand, found that mixtures of zinc oxide and chromium oxide, after heating to different temperatures, showed a greater sorptive power for dyes than either of the components alone, and that

---

[1] *Z. phys. Chem.*, 1931, **12 B**, 427, *Z. angew. Chem.*, 1932, **45**, 341.

[2] *Z. anorg. Chem.*, 1935, **223**, 297

their maximum capacity corresponded approximately with the greatest catalytic activity

In Fig. 65 the rate at which three typical dyes were taken up from methanol solution, for one particular catalyst, is

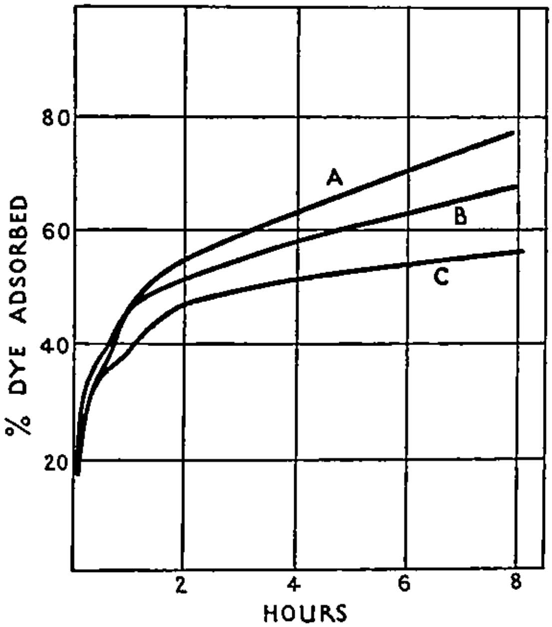


FIG. 65. Adsorption of dyes from methanol solution by zinc oxide-chromium oxide catalyst
A, Congo red.
B, Fuchsin.
C, Eosin.

illustrated, and comparative results were obtained by measuring the colour of the remaining solution after removal of the catalyst by means of a centrifuge, at the end of a given time. The adsorptive capacity of four series of catalysts is shown in Fig. 66 for fuchsin, and it is clear that, although there is a steady fall in the capacity of either component alone as the temperature to which it had been heated is raised, there is definite evidence of reaction in the case of mixtures of zinc oxide and chromium oxide. This conclusion is in good agreement with the results obtained by Huttig and his fellow investigators which are described on p. 175.

As the forces which lead to the taking up of dyestuffs by solid powders may be entirely different from those involved in the adsorption of gases, it is not to be anticipated that any general application of such methods will be successful in the study of catalyst areas.

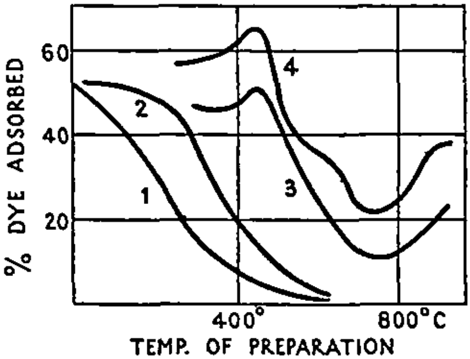


FIG. 66. Adsorption of fuchsin by zinc oxide-chromium oxide catalysts

1. Cr_2O_3 alone.
2 ZnO ,,
3. Mixture heated in absence of oxygen.
4. ,, ,, air.

Brunauer and Emmett[1] have applied adsorption measurements to the determination of the surface of an iron catalyst. It was found that the isotherms for nitrogen, oxygen, argon, carbon monoxide, and carbon dioxide at temperatures near the boiling-points of the various gases were all characterized by a relatively flat portion, shown in Fig. 67, which on extrapolation to zero pressure intercepted the ordinate at approximately the same point. It is suggested that this zero value indicates the amount of gas required to form a unimolecular layer. On this basis, and assuming close packing of the molecules, the calculated area of 46·2 gm. of catalyst was found to be between 17·6 and 20·6 square metres depending on whether the density of the solid or liquid form of the condensed gases was used. The results obtained with butane did not fall into line with the other gases.

It must be remembered, however, that although such a method of measuring total surface may be applied to any

---

[1] *J.A.C.S.*, 1935, 57, 1754.

catalyst, the figures obtained are not likely to have any relation to the area of the surface which is effective in any particular reaction, and it must be concluded that there is no simple relation between activity and surface area.

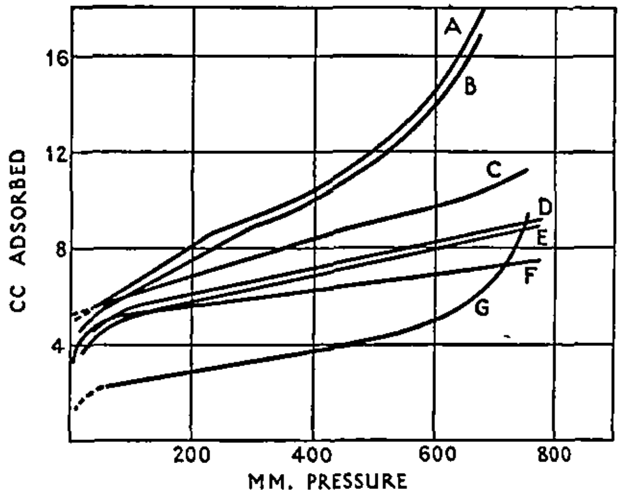


FIG. 67. Adsorption isotherms at low temperatures.

A, nitrogen at −195°
B, oxygen „ −183°
C, argon „ „
D, carbon monoxide at −183°
E, carbon dioxide at −78 5°
F, nitrogen at −183°
G, butane at 0°

Zero values by extrapolation of linear part are between 4 7 and 5 2 except for butane.

2. *Changes in density, or other physical properties.*

The determination of the true density of a catalyst after it has been used is not an easy matter, and errors may frequently be introduced owing to secondary changes in the surface, such as oxidation of a pyrophoric metal, or on account of the presence of large amounts of adsorbed gases. Audibert and Raineau[1] have given some attention to this question, and concluded that the density of an active catalyst is always less than that of an inert modification. In the case of a copper catalyst, they showed that an observed density

[1] *Compt. Rend.*, 1933, 197, 596.

of 7·60 was obtained, which is very appreciably less than the value of 8·9 calculated from the known dimensions of the crystal lattice. The X-ray pattern given by the active form also contained slight irregularities which disappeared on prolonged heating, and loss of activity occurred simultaneously. Further reference to the information provided by X-ray examination will be found in section 4 of this chapter

The effect of promoters on the density of a catalyst has been little investigated. Griffith and Hill[1] found that there was not a steady change in density, with increase in the quantity of promoter, in the case of molybdenum oxide catalysts containing added silica; the measurements were made after reduction in hydrogen at 450° for 50 hours in every case, with the results shown in Table 16. These figures suggest that the function of the silica, in the initial stages of its addition, is not that of a carrier, but that it actually takes a place in the crystal lattice of the solid. Beyond the saturation point for the amount of promoter which can be taken up in this way, the excess of silica is functioning as a diluent. It is particularly interesting to observe that the mixture of maximum density also coincides with that of greatest activity for the decomposition or the activated adsorption of hydrocarbons, as shown on pp. 39 and 40.

TABLE 16

Density of promoted catalysts

Catalyst	*Density*
100 Mo atoms with 0·0 Si . . .	6·19
" 3·0 " . .	6·23
" 4·4 " . . .	6·39
" 5·5 " . .	6·18
" 10·0 " . .	5·97

It is probable that density alone has little bearing on activity, but that when differences of this kind are observed they are to be regarded rather as indications of more fundamental changes in the character of the catalyst than as the ultimate cause of alterations in the activity. Similar comments apply in the case of other physical properties such as colour or, with substances such as mixtures containing iron,

---

[1] *P.R.S.*, 1935, 148 A, 194.

magnetic susceptibility. Huttig,[1] for example, found that, when mixtures of zinc oxide and ferric oxide were heated to different temperatures, their activity for the combustion of carbon monoxide showed two maxima. The higher of these corresponded with the appearance of paramagnetism and of a fluorescence different from that of zinc oxide. At the same time the density was a minimum, and crystallization of zinc ferrite was on the point of beginning.

3. *Chemical changes in the catalyst.*

The fact that active catalyst surfaces are rarely found ready made, but have to be obtained by the treatment of an alternative compound of the active element, introduces a good deal of uncertainty as to the chemical composition of the effective substance. This statement applies particularly to the case of catalysts prepared by the reduction of a metallic oxide, either to an intermediate state of oxidation or to the metal itself, and equally to the reverse process of partial oxidation of a metal or one of its lower oxides.

A number of illustrations will make these points clearer. Armstrong and Hilditch[2] investigated a series of nickel catalysts to which alumina and other oxides had been added, in varying amounts, as promoters. The activities of the mixtures were compared by their influence on the rate of hydrogenation of cotton-seed oil. A large change in the catalytic activity was observed as the chemical composition of the nickel surface was altered, and this was associated with differences in the colour of the catalyst. With nickel-alumina mixtures, for instance, the data shown in Table 17 were obtained; these are also presented in Fig. 49, and may be compared with illustrations of promoter action which have already been discussed (p. 72) and of carrier action (p. 88). Whether this is actually to be considered as an example of delayed dilution by means of a carrier or as incompletely explored promoter action, it is evident that the degree of reduction of the nickel oxide, which was used as the starting material, is of vital importance to the results and that it is greatly affected by the presence of very small quantities of another oxide.

---

[1] *Z. anorg. Chem.*, 1935, **223**, 241.

[2] *P.R.S.*, 1923, **103** A, 586.

TABLE 17

Addition of alumina to nickel

Per cent. Al_2O_3	*Colour of catalyst*	*Per cent. metallic nickel*	*Relative activity*
0·5	Black	80·7	105·1
1·0	,,	60·9	106·5
1·5	,,	57·7	106·4
2·0	,,	47·0	106·5
2·5	,,	34·3	104·4
5·0	Grey-black	4·5	98·3
10·0	Green with black particles	0·9	1·7
20·0	Green	Trace	1·3

Schmitt[1] also refers to extensive colour changes in nickel catalysts which were obtained by the reduction of the oxide at different temperatures. In the reverse direction Piggot[2] investigated the manganese dioxide catalysts used in the oxidation of ammonia to nitric acid. The oxide alone was changed from black to light brown during use, but if another oxide, such as silver oxide or copper oxide, was present, very little change in colour was observed, and the efficiency of the catalyst was considerably improved.

Again, differences have been observed[3] in the case of oxides of chromium and copper to which varying amounts of carrier have been added, as described in Chapter III. When precipitated chromium hydroxide was used as the catalyst for the dehydrogenation of dekalin at 500°, it was changed into the black oxide. On the addition of an inert carrier in quantities up to about 90 per cent. by weight the colour remained unchanged, and the catalytic activity also was not affected. When the dekalin was replaced by cyclohexane, however, the catalyst had an entirely different appearance after use, and was dark olive-green in colour. Addition of carrier to this material led to an immediate decrease in activity and in the intensity of the colour; with 90 per cent. of carrier the product was only very pale grey. If the black oxide, which had been previously obtained by treatment with dekalin, was used to decompose cyclohexane it was found to be practically

---

[1] *Z. phys. Chem.*, 1925, **118**, 193.

[2] *J.A.C.S.*, 1921, **43**, 2034.

[3] Griffith, unpublished data.

inert, having only about one-hundredth of the effect shown by the green oxide.

The evidence is thus convincing that catalytic activity may be highly specific, and belong to a particular compound rather than to a number of derivatives of a particular element.

The same point is emphasized by the example of copper catalysts which were also employed to dehydrogenate dekalin. The activity associated with metallic copper, which was prepared by reduction of the oxide, was found to correspond with the characteristic red colour. Immediately reduction of the oxide was not complete, as was the case when a high percentage of carrier was present in the mixture, there was a loss of activity and the appearance of the used catalyst was altered to black.

Similar colour changes were noticed with titanium oxide, where the addition of alkali prevented reduction of the light brown oxide to the active black oxide.

In attempting to follow chemical changes which take place on such surfaces during use, some difficulties are experienced in applying the usual analytical methods to the problem, as the important effects may be restricted to a very small proportion of the total catalyst material which is present. Measurements of the rate of reduction of ferric oxide, however, by G. B. Taylor and Starkweather[1] have shown that differences can sometimes be recognized. They found that the ignited oxide was not appreciably reduced at 350°, but that the gel was converted to Fe_3O_4; further reduction to metallic iron at 450° was accelerated by the presence of other metals such as copper, nickel, or silver, but greatly retarded by alumina or chromium oxide if these were admixed by co-precipitation.

Almquist and Black,[2] on the other hand, in their studies of the poisoning of iron catalysts used in ammonia synthesis, by means of oxygen (see p. 94), showed that, according to existing equilibrium data, normal iron surfaces should not be oxidized by hydrogen-steam mixtures containing less than 16 per cent. H_2O, whereas the catalytic iron retained oxygen from gas which contained it in concentrations as low as 0·008

---

[1] *J.A.C.S.*, 1930, 52, 2314.

[2] *Ibid.*, 1926, 48, 2184.

per cent. The iron atoms concerned in the poisoning (and also in the catalysis) must therefore be in a highly unsaturated condition, and it is evident that no assumptions can safely be made, on the basis of accepted equilibrium data, as to the state of reduction or oxidation of the active centres in the catalyst surface.

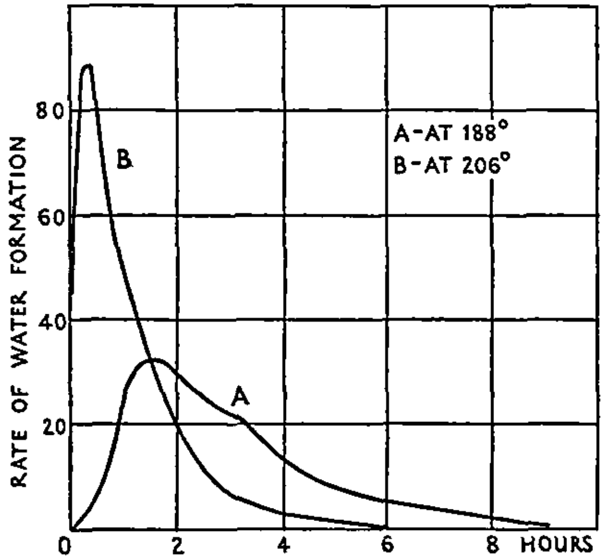


FIG. 68. Reduction of nickel oxide by hydrogen.

As long ago as 1916 Langmuir[1] suggested that heterogeneous reactions involving a solid phase on both sides of the equilibrium might occur mainly at the interface between the two solids, under which circumstances the change would be auto-catalytic and would increase up to a maximum velocity before finally decreasing. If, however, the two solids were completely miscible, the rate of reaction would depend on the surface area of the reacting solid and would fall off throughout the change. Benton and Emmett[2] investigated these points by studying the reduction of nickel oxide and ferric oxide, the former giving curves as shown in Fig. 68 and the latter those of Fig. 69; these correspond with the two possibilities discussed by Langmuir, and the reasoning is confirmed by the facts that no solid solutions are formed during reduc-

---

[1] *J.A.C.S.*, 1916, 38, 2263.
[2] Ibid., 1924, 46, 2728.

tion of nickel oxide,[1] while Fe_2O_3 and Fe_3O_4 are known to give solid solutions.[2] The possibility of differences in the course of the reduction of a metal oxide due to the presence of a different oxide are thus very great.

The presence of a second oxide may even lead to the production of a metal from its oxide at a temperature where it would remain unchanged if in a state of purity. Rogers[3] found that zinc oxide was reduced to the metal in the presence of copper oxide at temperatures where it was not attacked when alone. Ubbelohde[4] also has discussed the possibility of auto-catalytic effects in the reduction of metallic oxides, and concludes that this can be detected with copper and lead.

It must not be supposed, however, that the addition of other materials to the oxide undergoing reduction will invariably lead to accelerated formation of the metal. Schenck and his fellow investigators[5] found that iron catalysts as used for the synthesis of ammonia are more easily oxidized, and that iron oxide is less quickly reduced when substances such as magnesia, lime, silica, alumina, or titanium oxide are present; these observations fall into line with those of Almquist and Black.

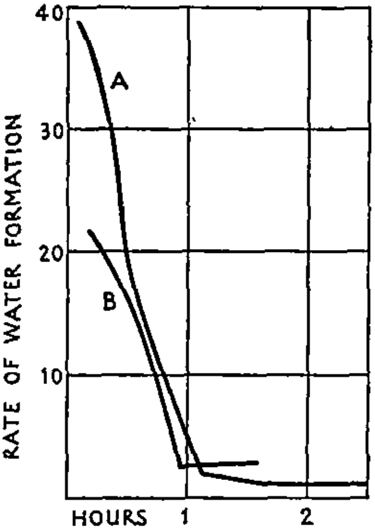


FIG. 69. Reduction of ferric oxide by hydrogen.

A, precipitated oxide, at 285°.
B, oxide from nitrate, at 300°.

Reference has already been made, in Chapter II, to the fact that the reduction of metallic oxides takes place with different velocities when hydrogen and deuterium are compared. There is, however, no evidence that the degree of reduction attained

---

[1] Wöhler and Balz, *Z. Elektrochem.*, 1921, 27, 413.

[2] Sosman and Hostetter, *J.A.C.S.*, 1916, 38, 807.

[3] *J.A.C.S.*, 1927, 49, 1432.

[4] *T. Farad. Soc.*, 1933, 29, 532.

[5] *Z. anorg. Chem.*, 1929, 184, 39; 1932, 206, 129, 273.

under equilibrium conditions, nor the catalytic activity of the surface obtained, varies with the particular isotope employed.

Adsorption and chemical composition. In view of existing ideas concerning activated adsorption it is to be expected that the behaviour of individual compounds in this respect would be highly specific. Kingman[1] showed that this happened with mixtures of zinc oxide and chromium oxide which were examined at varying stages of reduction. When hydrogen was admitted to the unreduced material, adsorption and reduction both took place even at 0°, and similar results were obtained when carbon monoxide was used. Some typical figures obtained in these experiments are given in Table 18, where the amount of hydrogen consumed indicates the progress of reduction of the oxide. Curves showing the change in rate of adsorption at 100° with various stages of reduction are also given in Fig. 70. It can be seen that the rate of adsorption first falls, but then increases again as the amount of hydrogen consumed as water decreases. The changes must be ascribed to disappearance of one type of active centre by reaction with hydrogen, more quickly than the new type is formed; towards the end of the reduction, however, the new oxide surface has a much greater effect.

TABLE 18

Adsorption of hydrogen during reduction of oxide catalyst

Hydrogen consumed, c.c.	*Hydrogen adsorbed, c.c. in 4 hours*
0·56	1·64
3·02	1·535
8·13	1·38
27·1	0·865
44·7	0·72
63·2	1·05
66·8	1·19
69·0	1·23

The determinations of heats of adsorption carried out by Garner and Veal[2] with hydrogen and carbon monoxide on mixtures of zinc and chromium oxides led to the same conclusions. It was found that on the catalyst which had been

---

[1] *T. Farad. Soc.*, 1931, 27, 654.

[2] *J.C.S.*, 1935, 1487.

thoroughly reduced with hydrogen the adsorption of either hydrogen or carbon monoxide was reversible, and had a gradually decreasing heat effect as saturation was approached. On the unreduced catalyst the heat effects were much larger, the adsorption was irreversible, and water or carbon dioxide were the main desorption products. Chemical changes also occurred in the catalyst, and the ratio of hydrogen consumed in the reduction to that held by adsorption gradually increased.

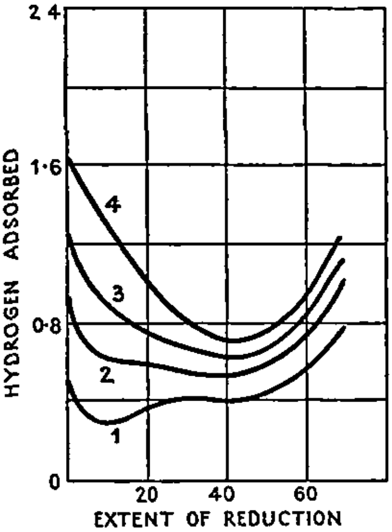


Fig. 70. Adsorption on slowly reduced catalyst.
1, figures after 0·05 hours.
2, ,, 0·3 ,,
3, ,, 1·0 ,,
4, ,, 4·0 ,,

Chemical changes due to poisons. The fact that permanent poisoning of a catalyst occurs when a new and stable compound is formed at the surface has already been emphasized. It is accordingly not difficult to understand why oxide and sulphide catalysts, which are now so extensively employed in large-scale operations, are much more resistant to poisoning than the older type of material such as finely divided nickel The question is essentially one of the stability of the surface towards chemical attack by substances which may be present in any of the reactants passing over it.

An interesting observation by Varga[1] constitutes a case which is the very reverse of poisoning, and which again is due to the chemical state of the catalyst surface. It was found that, if molybdenum oxide was used to accelerate the hydrogenation of tar oils and similar substances at temperatures of about 450° and under pressures of the order of 200 atmospheres, the activity of the catalyst was actually increased by the presence of free hydrogen sulphide in the reaction gases. Similar results are recorded in the hydrogenation of coal tar

---

[1] B.P. 313,505.

under high pressure[1] for the system containing excess sulphur over the amount required to form molybdenum sulphide. These effects are due to the fact that the sulphide has a greater catalytic activity than the oxide, and that it is only stable, under the extreme conditions of temperature and pressure which were used, in the presence of a definite pressure of hydrogen sulphide. The situation is, in fact, precisely parallel with that existing when water is present in the mixture of nitrogen and hydrogen circulated over iron catalysts for ammonia synthesis, but the effects happen to be harmful in one case and beneficial in the other.

4. *The crystal structure of catalysts.*

The fact that methods of preparation may have a profound effect on the properties of a catalyst has been emphasized in the first chapter, and some further points in this connexion have now to be discussed. The activity of titanium oxide prepared by ignition of the precipitated hydroxide has, for instance, been examined by Rudishill and Engelder,[2] and it was found that the lower the temperature of ignition the higher was the activity. The particular salt from which the hydroxide was precipitated also had some effect, and thorough washing of the precipitate was found to give better results. In the case of chromium oxide catalysts used for hydrogenation of ethylene or propylene, Lazier and Vaughen[3] found that Cr_2O_3 obtained by precipitation or by vacuum ignition of ammonium bichromate was a good catalyst, but if prepared by ignition of the nitrate and oxalate, or by reduction of a higher oxide, the material was crystalline and inactive.

These facts suggest that the structure of the catalyst compound may have a considerable influence on its properties. The application of X-rays to the investigation of catalysts has, in fact, revealed that they are almost invariably crystalline in character, although this statement must not be taken as excluding the possibility of amorphous material also being present.

---

[1] *F.R B. Annual Report,* 1932, p. 45

[2] *J Phys. Chem*, 1926, **30**, 106.

[3] *J.A.C.S.*, 1932, **54**, 3080.

The type of lattice to which a structure belongs has been shown by Long, Frazer, and Ott[1] to be a significant factor in metal catalysts which were used for the conversion of benzene to cyclohexane. Mixed or single-component metallic surfaces were prepared by the reduction of precipitated hydroxides, and those products which had exclusively body-centred structures were found to be inactive or only to show very minor effects, while those which had a face-centred lattice were active. The investigations of Hagg[2] and of Eisenhut and Kaupp[3] have also revealed analogies between the lattice dimensions of iron crystals and their behaviour towards nitrogen.

The latter authors found that γ-Fe with the minimum inter-atomic distance 2·52 Å took up nitrogen, while α-Fe having the distance 2·478 Å only did so very much more slowly, and when this occurred the distance between iron atoms was increased to 2·5 Å. As further quantities of nitrogen were absorbed, the γ-Fe lattice structure was gradually adopted at temperatures well below the normal transition point. These facts led to the suggestion that the active parts of the iron catalyst surface were those in which abnormal lattice spacings were present.

The fact that the crystal structure of a catalyst, rather than its atomic nature, may determine the activity is revealed by the discovery of Storfer,[4] that cyclohexane was decomposed to benzene and hydrogen in contact with graphite, but remained unchanged by diamond under similar conditions.

Promoters and compound formation In the discussion of promoted catalysts it has already been pointed out that the use of X-rays can indicate quite clearly the formation of compounds, but that they do not provide any explanation of promoter action. Wagner, Schwab, and Staeger[5] have come to the following general conclusions on this subject. in cases where the activity of a catalyst is increased by the addition of a second component this may be due to one of three

---

[1] Ibid , 1934, **56**, 1101.

[2] *Z phys. Chem* , 1930, **8** B, 455, 1931, **12** B, 32.

[3] Ibid , 1928, **133**, 456, *Z. Elektrochem* , 1930, **36**, 392.

[4] *Z Elektrochem.*, 1935, **41**, 541.

[5] *Z. phys. Chem* , 1934, **27** B, 439

causes: (1) Structural changes in the active component are prevented at high temperatures, as in mixtures of copper oxide with zinc oxide; (2) new types of active centre are formed in the mixture, as occurs with the addition of magnesium oxide to copper oxide; or (3) compound formation takes place. The latter only will be revealed by X-ray examination, both the other conditions showing the lines characteristic of the unchanged lattices of both components.

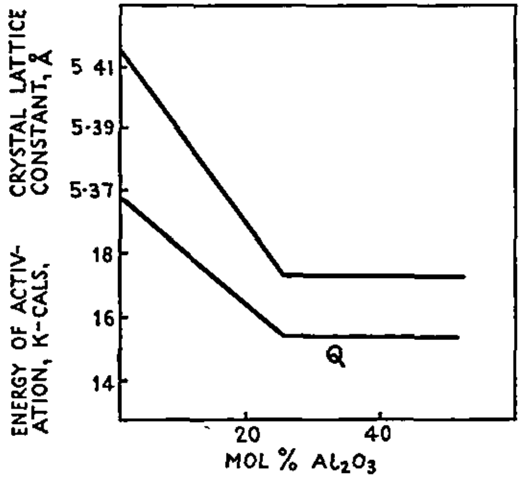


FIG. 71 Variation of lattice constant and activation energy for combustion of carbon monoxide on iron oxide-alumina catalysts

Eckell,[1] however, as shown in Fig. 71, found that the energy of activation for the reaction of carbon monoxide with oxygen in contact with catalysts consisting of mixtures of iron oxide and alumina was influenced by the lattice dimensions of the material, and in the hands of Huttig and his co-workers[2] X-ray methods of examination have given results which are of great interest.

As examples of the extensive investigations which have been carried out in this connexion, the cases of zinc oxide and of magnesia-ferric oxide and cadmium oxide-ferric oxide

---

[1] *Z. Elektrochem.*, 1932, **38**, 918.

[2] *Z. anorg. Chem*, 1934, **217**, 22; *Kolloid-Z.*, 1934, **67**, 265; **68**, 253; *Kolloid Beihefte*, 1934, **39**, 277, *Z. Elektrochem*, 1934, **40**, 306, and many others.

mixtures may be considered. Zinc oxide catalysts were prepared from the oxalate, carbonate, and nitrate, and were studied with respect to their activity, crystal structure, solubility, and density. It was found that the distinctive properties of the various forms were not due to modifications in the crystal structure nor to the presence of an amorphous phase, but to the occurrence of faults in the crystals, to the distribution of the crystal planes over the total surface, and to the nature of the pores in the mass.

In the case of zinc oxide catalysts used for the decomposition of methanol, Schleede, Richter, and Schmidt[1] found that the form which was obtained by heating the nitrate at 360° was inactive, while that prepared from the hydroxide or the carbonate was very efficient. The former was shown to be luminescent on account of the presence of twinning planes in the mass of compact particles, but the latter was much less compact, more porous, and did not luminesce.

With mixtures of magnesium and ferric oxides the changes which took place on heating them to different temperatures were traced with respect to their catalytic effect on the oxidation of carbon monoxide. The maximum activity was produced by treatment at 625°, and at this temperature the X-ray diagram showed that the formation of magnesium ferrite aggregates was just beginning, but that the bulk of the mixture had not reached the stage of compound formation.

Experiments on mixtures of cadmium oxide with ferric oxide were carried out on an even more comprehensive scale.[2] The components were ground to pass a sieve of 10,000 mesh to 1 sq. cm., and then heated to different temperatures for fixed periods. The catalytic activity, magnetic susceptibility, colour, and density were determined on the products. It was discovered that below 450° no changes took place, but that between 450° and 550° the activity rose sharply and then fell again, reaching zero at 800°. The colour altered from brown at 450° to yellow at 600°, brown again at 750°, and violet at 1,000°, while the magnetic susceptibility only changed

---

[1] *Z anorg. Chem.*, 1935, **223**, 49.

[2] *Act. Physicochim.*, 1935, **2**, 129.

above 700° to a maximum at 750° and then decreased rapidly.

The loss of catalytic activity after high temperature treatment was found to be due to extensive formation of the compound $Cd(FeO_2)_2$, and the active parts of the catalyst were considered to be the phase boundaries between the component oxides and the ferrite. It is evident from these investigations that changes in the physical properties of the catalyst may take place without appreciably affecting its activity.

Empty spaces in crystal lattices. Some experiments which have been carried out by Hagg[1] in connexion with the possibility of the existence of empty spaces in crystal lattices, appear to be of particular significance with relation to the structure of active catalysts and to the mechanism of promoter action. It was demonstrated that the colour of sodium tungsten bronzes of the general formula Na_xWO_3 changed as the value of x varied, and that variations in the dimensions of the crystal lattice occurred. Oxidation of pentavalent to hexavalent tungsten also led to deepening of the colour and to an increase in the number of empty spaces in the lattice; in the blue form of the compound as many as two-thirds of the sodium positions might be vacant.

Similar effects were observed in the cases of certain hydrides, carbides, and nitrides of the transition elements in the periodic system, and in structures of a spinel type. When the system $MgO . Al_2O_3$, for instance, dissolved more alumina, vacant places appeared in the lattice, and when Fe_3O_4 was oxidized to γ-Fe_2O_3 only eight-ninths of the iron positions were occupied. Such empty spaces are probably associated with very special adsorptive properties, and a much closer study of their behaviour would undoubtedly prove very profitable. It is significant that a great many catalytic materials are prepared by reactions involving a change in valency or in the degree of saturation of valency bonds, and also that density determinations with promoted catalysts suggested that the promoter might take a place in the catalyst crystal (p. 112).

---

[1] *Nature*, 1935, **135**, 874; *Z. phys. Chem*, 1935, **29** B, 192.

5 *The structure of the surface layers.*

Although X-ray examination generally fails to account for the differences produced by additions of small quantities of a second component to catalysts, other means are available for inspecting the outside layers of materials, which do not penetrate nearly so far into the molecular structure as is the case with X-rays The two methods of greatest practical importance are (1) electron diffraction exploration, and (2) microscopic examination.

Electron diffraction methods. Although this method of examination is only in its infancy, the information which it may reveal is indicated by the work of Finch and others[1] on sputtered platinum catalysts, used in the interaction of hydrogen and oxygen. Their activity was found to depend on the conditions of preparation, but the X-ray diagrams revealed no differences. In some instances an induction period was observed before the reaction set in; in others the change began at once, or again there might be complete absence of catalytic effect. The films which showed an induction period were obtained by sputtering in oxygen and were always yellow in colour, while the active form was black or metallic and opaque. Films showing an immediate activity were given by prolonging the time of sputtering, and completely inactive forms by operating with a high cathode temperature. Electron diffraction patterns obtained from the various forms showed that PtO_2 rings were present in the active catalyst, without any Pt rings in the form which had an induction period. No oxide rings were given by the inactive films. Microscopic examination showed that the conversion of an inactive into an active surface started from a few active spots already present, the colour changes which appeared when hydrogen was admitted to the system being clearly visible. When the metal film developed fissures and cracked away from the substrate it became catalytically inactive.

A series of later papers by Finch and his co-workers[2] give detailed descriptions of the camera and the experimental

---

[1] *P R.S*, 1933, **141** A, 414.

[2] Ibid, 1934, **145** A, 676; *Proc. Phys. Soc.*, 1934, **46**, 148, *T. Farad. Soc.*, 1935, **31**, 1051

methods employed, and also some important developments in their application. It has been found that extra rings will appear in the pattern of a surface due to the entry of extraneous gas into the crystal lattice. For instance, gold on heating in air at 300° gave a series of extra rings which gradually disappeared on heating the specimen *in vacuo.* The results were not due to the formation of normal compounds, as the rings have different characteristics and are also stated to be produced on heating gold in argon, but the condition of the surface appears to be intermediate between simple adsorption and true compound formation. The possible significance of such observations in connexion with the study of surfaces in contact with gases is obvious, but it is also clear that the technique is difficult and that the proper interpretation of results is not easy.

Mark, Motz, and Trillat[1] have indicated that extra rings may occur in the patterns from metal surfaces owing to the presence of traces of grease, and it has been observed by Finch and Quarrell[2] that similar effects may be caused by amalgamation with mercury. Although the former can be fairly easily separated from those due to adsorbed gases, the amalgam extra rings are much more difficult to isolate, and rigid precautions are necessary to exclude the possibility of experimental errors arising from these causes.

Electron diffraction methods can also be used to follow the growth of crystals or the deposition of a film on a substrate, and it has been found that such a film can be greatly distorted.[3] Silver deposited on a copper crystal, for instance, follows the orientation of copper although with normal silver spacings, and a surface film of oxide may follow the crystal form of the underlying metal. The Beilbey layer on a metal also often has the property of dissolving metallic films which would not be soluble in the crystalline surface.

It is to be expected that the extension of such methods of examination to the study of mixed or promoted catalysts would give information of the greatest value.

Microscopic inspection of catalysts. Observation under the

---

[1] *Naturwiss.*, 1935, **30**, 319.

[2] *Nature*, 1935, **136**, 720.

[3] Thomson, *P.R S*, 1931, **133** A, 1.

microscope is a particularly rapid and convenient method of which permanent records can easily be obtained by photography. In questions of determining particle size direct measurement is also possible, but one of the most interesting developments of this technique is in the study of thin films. Further reference to this point is made in the section where the mobility of surfaces is discussed (p. 130).

6. *Other factors affecting the properties of surfaces.*

In order to determine whether hydrogen in contact with an active catalyst was present in molecular or atomic form, Wolfenden[1] extended earlier experiments of Gauger[2] and measured the ionization currents of copper and nickel surfaces in the presence of hydrogen at low pressures; the results showed that atomic hydrogen was present, but the effects were very similar with active and inactive forms of metal surface. In later experiments of Finch and Bradford[3] mixtures of carbon monoxide and oxygen were passed over heated gold gauze which was electrically insulated, and measurements were made of reaction velocity, rate of charging of the surface, and its equilibrium potential. It was found that changes in catalytic activity, and modifications in the character of the surface film, were paralleled by alterations in the rate of electrical charging. Similar experiments with silver showed that the behaviour of this catalyst depended largely on its previous treatment, as it only altered slowly when conditions were changed. The relation between the rate of charging of the surface and its catalytic activity was again detected, but the equilibrium potential only indicated the composition of the film adsorbed on the metal. At low temperatures the effect of the surface on the potential it acquires is highly specific, as shown in Table 19, where the values of the instantaneous maximum current i_0 flowing from the surface at the moment of insulation is given for platinum, gold, and nickel.[4] At higher temperatures the value of the surface potential is determined by the nature of the gas rather than the surface; this fact may be compared with the

---

[1] *P.R S.*, 1925, **110** A, 464.

[2] *J A C.S* , 1924, **46**, 674

[3] *P.R S.*, 1934, **144** A, 320.

[4] Stimson, *P R.S.*, 1934, **144** A, 307.

observation that differences between the activity of various catalysts disappear at sufficiently high temperatures.

TABLE 19

Instantaneous currents characteristic of different surfaces

Surface at 850°	$i_0 \times 10^{11}$ *amps.*					
	H_2	*Vacuo*	O_2	A	CO	N_2
Pt	20·0	26 67	11 27	8 0	2 0	9·33
Au	17 6	13 33	5 33	4 03	2 53	2 0
Ni	10 6	7 36	5 00	4·53	7 07	4 32

The photo-electric properties of iron and platinum in the presence of different gases were determined by Brewer,[1] who found that the results were different from those given by the pure metals under good vacuum conditions, the emissivity of the surface increasing rapidly as the gases were admitted. This behaviour closely resembled that of a surface known to contain ions, such as one of iron and potassium.[2] Brewer also pointed out[3] that ions on a surface have a large effect on the work function for escaping electrons, and that chemical reaction might be located at points of lowest critical increment; experimental evidence gave qualitative support to this idea in that ammonia was found to be more strongly ionized on an iron catalyst than on platinum, and the activity of the former for its decomposition was considerably greater. There is, however, no evidence that ionization is essential to catalysis.

The relation between photo-electric emission from surfaces and the nature of the adsorbed layer is fully dealt with in de Boer's book, *Electron Emission and Adsorption Phenomena* (Cambridge, 1935), to which reference should be made.

Measurement of electron emission from a surface has been used by Johnson and Vick[4] to determine high-velocity approach to chemical and physical equilibrium. Changes occurring in layers of unimolecular thickness may have a very considerable velocity on account of the simultaneous exposure of all the molecules. In order to follow such changes

---

[1] *J.A.C.S.*, 1932, **54**, 1888.

[2] Ibid., 1931, **53**, 74.

[3] *J. Phys. Chem.*, 1928, **32**, 1006.

[4] *P.R.S.*, 1935, **151A**, 296, 308.

a cathode-ray oscillograph was employed, the track of the oscillograph spot being recorded photographically as it responded to changes in potential across a high resistance carrying the thermionic current from the filament under examination. It was found that the duration of oxygen on a tungsten filament varied from 3·49 sec. at 2,362° Abs. to 0·36 sec. at 2,548° Abs.

The application of this technique to a number of other surfaces and gases should provide very interesting results.

Loss of catalyst activity. Apart from cases of retardation or poisoning, which are separately considered, loss of activity may be due to physical changes in the catalyst itself. Eckell,[1] for example, has examined the behaviour of nickel foil for the hydrogenation of ethylene, and has found that cold working increased the activity with simultaneous deformation of the crystal lattice, but that on heating the activated metal recrystallization occurred and led to a loss of activity.

In the case of nickel catalysts used by Fajans[2] for the conversion of para-hydrogen, it was found that sintering began at a lower temperature the higher the activity of the catalyst had been initially. Dobytschin and Frost[3] showed that the ageing of palladium catalysts was related to the growth in particle size.

A relationship between the loss of catalytic activity and the disappearance of pyrophoric properties has been detected by Tammann.[4] A metallic nickel catalyst was heated to different temperatures and then tested for the conversion of para- to ortho-hydrogen at 15°; the time of half-change altered as shown by the curves of Fig. 72 for two different samples of which 1 was originally more active than 2. It was also observed that pyrophoric metallic nickel was obtained when nickel oxalate was heated at 350° in hydrogen, but when the preparation was carried out at 390° the product was no longer pyrophoric. These facts indicate that the incipient loss of catalytic activity and the disappearance of the pyrophoric form occur in the same temperature range,

---

[1] *Z. Elektrochem.*, 1933, **39**, 423, 433.

[2] *Z phys. Chem.*, 1935, **28** B, 252.

[3] *Act. Physicochim*, 1934, **1**, 503.

[4] *Z. anorg. Chem.*, 1935, **224**, 25.

and both depend on the changes which are produced in the metal surface by heating.

A closer study of the mobility of thin films of solids has been made by Andrade,[1] in the case of silver and gold deposited by sputtering, by the application of microscopic methods. Examination in this way was found to have some advantages over electron diffraction exploration as it gave data concerning the size of crystallites, but the two should rather be regarded as complementary. The films used were initially about 50 atoms thick and were heated *in vacuo*; the first crystallization was detected at 250–280° in the case of silver and at 400° for gold. The new particles consisted of spherulites which were much thicker than the remainder of the film, so that migration must have taken place in the surface. When the temperature was raised still higher the particle size increased, and definite crystalline shape developed; simultaneously patches, where the metal layer was extremely thin, appeared on the remaining parts of the surface. The presence of traces of mercury increased the mobility of the metal to such an extent that crystallization could be detected at room temperatures.

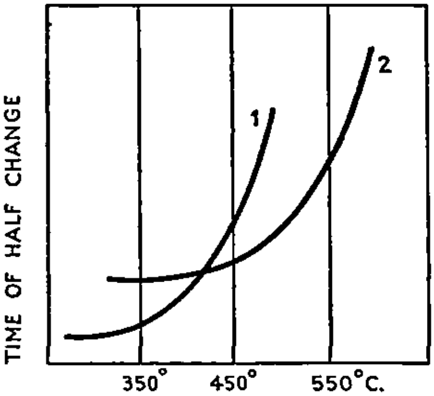


FIG. 72. Effect of sintering at different temperatures on the activity of nickel catalysts for conversion of para-hydrogen at 15°; catalyst 1 initially more active than 2.

As regards the action of promoters in suppressing particle

---

[1] *T. Farad. Soc.*, 1935, 31, 1137.

growth, some caution is necessary in the interpretation of experimental data. In the case of chromium oxide catalysts used in the dehydrogenation of dekalin, for example,[1] the activity-time curves given in Fig. 73 relate to the oxide alone, the promoted oxide which contains the optimum amount of silica, and the oxide to which 90 per cent of magnesium oxide has been added. It will be seen that the latter shows a steady activity throughout when calculated on the basis of the final catalyst volume, but that both the others take several hours to reach a steady value. The differences, however, are undoubtedly due to a slow reduction of a higher chromium oxide which is not accelerated by the presence of promoter, but which takes place more rapidly with the diluted catalyst containing magnesia. There is also the factor of shrinkage involved, in the three examples mentioned, changes in catalyst volume and activity during the determinations were as shown in Table 20. It is clear that with the

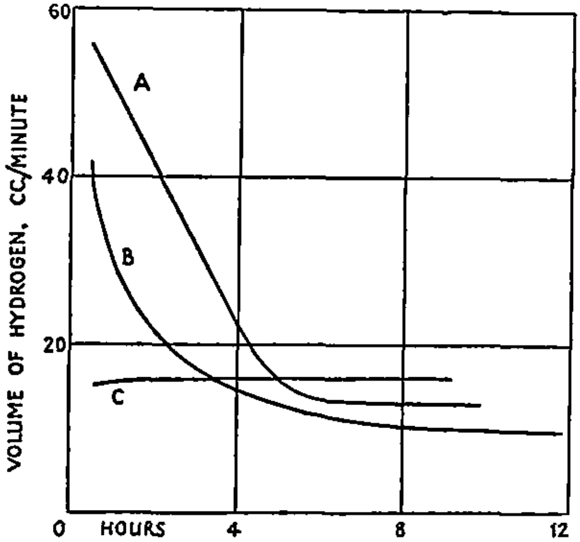


FIG. 73. Change in activity of chromium oxide catalysts with time
A, promoted catalyst
B, unpromoted oxide.
C, 10% oxide with 90% carrier.
No corrections for catalyst volume are made.

---

[1] Griffith, unpublished data.

catalyst containing a high percentage of carrier there is actually a slight increase in activity, when allowance is made for shrinkage, during the early stages of the experiment, but that in both the other examples an intrinsic loss of activity, as well as a decrease in catalyst volume, has taken place.

TABLE 20

Changes in catalysts during use

	Chromium hydroxide	*Chromium with silicon*	*10% Chromium hydroxide, 90% Magnesia*
Initial volume, c.c.	20	10	19
Final volume, c.c.	7·8	4·8	16 2
Initial activity	680	1,190	99
Initial activity corrected	265	570	85
Final activity	103	271	99

This example is accordingly similar to that described by Kuentzel,[1] in which hopcalite catalysts used for the oxidation of carbon monoxide were found to undergo a slow loss of activity on account of gradual reduction of a component oxide by means of the carbon monoxide.

Surface combustion and catalysis. Certain analogies have been observed between the effect of adding small quantities of a second oxide to refractory materials such as those employed in gas mantles or in surface combustion furnaces, and the action of promoters on catalyst activity. The experiments of Swan[2] and of Goggs[3] showed that the mixture of 1 per cent. cerium oxide with 99 per cent. of thorium oxide, which was most effective for use in incandescent mantles, was also the best catalyst for the combustion of either hydrogen or carbon monoxide.

At the same time the effects of refractory materials for other types of surface combustion are largely non-specific, and it is very doubtful whether the phenomena should be classified as examples of catalysis. It is also to be anticipated that differences of activity would largely disappear at such high temperatures, so that little could be learned concerning catalytic processes by a closer study of these cases.

[1] *J A.C.S,* 1930, 52, 445. [2] *J.C.S.*, 1924, 125, 780. [3] Ibid., 1928, 2667.

CHAPTER VI

GEOMETRY OF THE CATALYST SURFACE

THE facts presented in the previous chapter have been concerned more with the methods of experimental investigation and with the general results obtained than with the behaviour of individual molecules in contact with the surface. Before the phenomena of catalysis can be understood it is necessary to go farther than is possible by discussion of average effects, and to consider the conditions which may exist in different parts of a small surface.

In the theoretical treatment of the subject there are two main lines of approach. One of these is to investigate the kinetics of a number of typical reactions which take place on catalyst surfaces, and to compare them with the same changes taking place in homogeneous systems. At the same time information on the energy relations which exist during adsorption, activation, and desorption of molecules on or from the catalyst will be of very great assistance in understanding the conditions. It is proposed to set out the facts which are available in this direction in the next chapter.

The other method of approach, which is the subject of this chapter, is to study the actual configuration of the solid catalyst and to investigate the spatial arrangement of the adsorbed molecule on it; this may be described as the geometry of the surface. The term will be made sufficiently elastic to include the subject of affinity between the reactant and the catalyst molecules.

The concept of active centres.

A gradually increasing weight of evidence as to the lack of uniformity of the catalyst surface led H. S. Taylor to put forward the idea of active centres,[1] that is to say, specific limited parts of the surface which have a very high activity. The constituent atoms of these parts were imagined to be very loosely attached to the bulk of the catalyst so that their

---

[1] *P.R.S.*, 1925, 108 A, 105.

valency bonds were not completely satisfied. Variations in degree between the most active and quite inert parts of the surface were also to be expected.

In support of such views are the following facts: (1) the catalyst surface is sensitive to heat, so that it sinters and loses activity at temperatures considerably below the normal melting-point of the component; (2) chemical combination takes place between the catalyst and a gas under conditions where the massive component would not react, as for example in the case of iron catalysts and oxygen described on p. 115; (3) the surface is often poisoned by very small concentrations of an impurity, and the adsorption of different gases is affected to varying degrees by the same poison; (4) the heat of adsorption of a gas on the catalyst is not uniform, nor is the heat of activation of adsorption on the surface; (5) different parts of the surface are involved in specific reactions. Most of these points have already been fully discussed in earlier chapters, but further consideration must be given to some of them.

Change in activity at the melting-point.

Steacie and Elkin[1] have found that the activity of metallic zinc for the decomposition of methanol does not show any sudden decrease at the melting-point, nor does the order of the reaction change, and they suggest that this provides evidence against the existence of active centres. It must be remembered, however, that surface changes, leading to loss of activity, always occur well below the melting-point, and that no sudden change of efficiency is to be expected under such circumstances even if active centres do exist on the metal surface at lower temperatures.

The measurements of Bowden and O'Connor,[2] concerning the increase of accessible area on the solidification of a fused metal or alloy, also indicated that the changes at this point were small. It was found that the accessible area of unit surface of all liquid metals, used as a cathode for the displacement of hydrogen from dilute acid, was the same; if this

---

[1] *P.R.S.*, 1933, **142** A, 457; *Canad. J. Res.*, 1934, **11**, 47.

[2] *P.R.S.*, 1930, **128** A, 317.

was taken to be 1·0, then solidified gallium had an area of 1·7 and an alloy 1·4. On the other hand the solid after rubbing with glass paper increased in accessible area to 6·3, and on etching with nitric acid to 800 or 1,000.

Poisoning.

The early evidence of Vavon and Husson, discussed on p. 98, suggested that very material differences in the activity of various parts of the surface were revealed by progressive poisoning. Although the later experimental evidence of Maxted is against such extreme views, it is still clear that relatively small quantities of poison are required to produce a large decrease in activity, and that the first portions of poison added are much more effective than those at higher concentrations (see Fig. 62). Some additional evidence as to the existence of stepwise poisoning is also provided by Yoshikawa,[1] who found that a nickel catalyst could be poisoned by nickel sulphate so that reduction of the nitro group in nitrobenzene could still be carried out although hydrogenation of the benzene ring was suppressed.

Heats of adsorption and activation.

Difficulties associated with direct measurement of heats of adsorption have already been described in Chapter II. Many early records, which showed large alterations in the values observed during gradual saturation of the surface, must therefore be ignored as evidence for the existence of active centres. Fryling, for instance,[2] found that the heat of adsorption of hydrogen on nickel catalysts rose from a low initial value to a maximum, as shown in Fig. 74, and then decreased as the surface was covered. An attempt was made to explain this phenomenon by assuming that dissociation of molecular hydrogen into atoms took place on the most active parts of the catalyst, and involved an endothermic change which counteracted the exothermic adsorption effect. It now appears very doubtful whether such a maximum has any real existence. Rideal,[3] on the other hand, found that the corrected

[1] *Bull. Inst. Phys. Chem. Res. Japan*, 1934, **13**, 1042.

[2] *J. Phys. Chem.*, 1926, **30**, 818.

[3] *P.R.S.*, 1930, **127** A, 260.

heat of adsorption was independent of the quantity of gas adsorbed but dependent on the specific activity of the catalyst. Similar observations are recorded by Ward[1] and by Beebe[2]; examples of experimental results are given in Table 21 for the adsorption of oxygen and hydrogen on platinum. Maxted and Hassid[3] also found steady values for the adsorption of hydrogen on platinum.

TABLE 21

Heats of adsorption on platinum

	Total c.c. adsorbed	*Differential heat of adsorption K-cals. per gm. mol*
O_2 *on 11 gm.*	0·57	16·6
	1·10	16·5
	1·73	15·8
	5·20	16·0
	13·0	17·2
	16·6	17·2
H_2 *on 12 gm.*	0·22	62·5
	0·47	61·0
	1·38	70·0
	2·14	61·0
	3·49	62·5
	4·01	62·5
	4·54	60·0

At the same time there appears to be clear evidence that in certain cases, even with the most strict precautions in experimental technique, a gradual falling off in the heat of adsorption can be detected. Bull, Hall, and Garner[4] observed this in the case of adsorption of oxygen on charcoal, as shown in Fig. 75. If the gas was admitted to the adsorbent without special precautions, an apparent maximum in the heat of adsorption was detected, but by adopting a modified apparatus and allowing the gas to come into contact with the centre of the charcoal mass the steadily decreasing values shown were obtained. Although adsorption on charcoal is not strictly comparable with that of other gases on catalysts in general, the same type of curve has been found with other surfaces. Garner and Kingman[5] carried out very careful

---

[1] *P.R.S.*, 1931, **133** A, 506.

[2] *T. Farad. Soc.*, 1932, **28**, 761.

[3] *J.C.S.*, 1931, 3313.

[4] Ibid, 837.

[5] *T. Farad. Soc.*, 1931, **27**, 322.

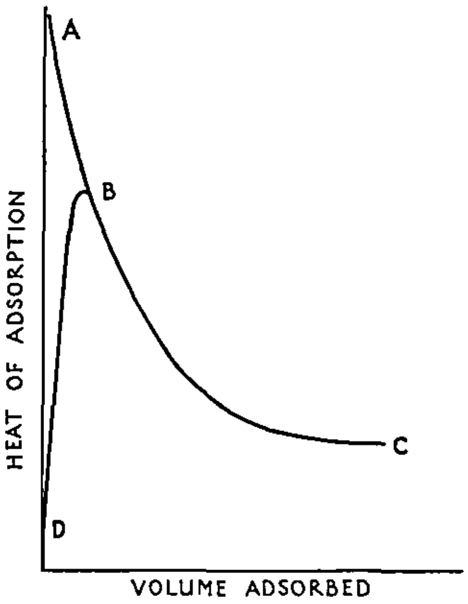


Fig 74 Heat of adsorption

DBC, observed curve
ABC, ideal curve with no dissociation.
Total heat of adsorption = area bounded by curve.

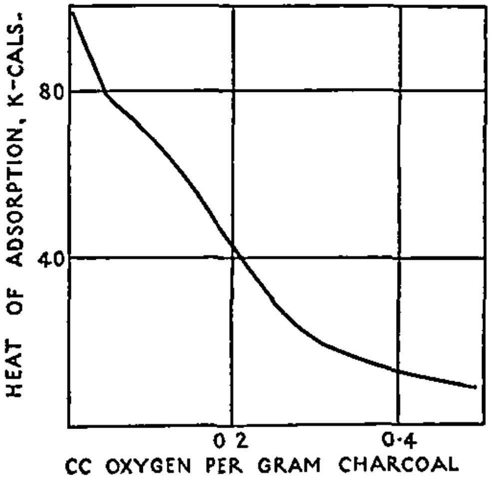


Fig. 75. Heat of adsorption of oxygen on charcoal.

determinations with hydrogen and carbon monoxide in contact with zinc oxide, chromium oxide, and mixtures of the two. The maximum heat of adsorption was observed with the first portions admitted, and the figure fell to about half its initial value when saturation was nearly complete.

It is perhaps significant that this example is found with oxide catalysts and not with a metal surface, but it must be remembered that the experiments of Roberts (p. 23) on the adsorption of gases by clean tungsten wire indicated a change in the heat of adsorption as saturation of the surface proceeded. This was due to interference caused by portions of gas which were already adsorbed, so that the results of measurements of heats of adsorption must not be regarded as final proof of the presence of inequalities in the catalyst surface. More numerous determinations of heats of adsorption of gases at elevated temperatures are desirable.

Beebe and Wildner,[1] by using a modification of the calorimeter described by Garner, subsequently made the very interesting observation that decreasing values of the heat of adsorption may occur with one particular gas but not necessarily with another. When carbon monoxide was adsorbed on a copper catalyst the differential heat of adsorption fell as saturation proceeded, but the adsorption of hydrogen on the same surfaces showed no such decrease. The possibility of other catalysts exhibiting a similar behaviour appears to be well worth investigation.

As regards the apparent energy of activation of the activated adsorption process, the evidence is much clearer; in every case examined the quantity is very considerably less in the early stages of saturation. The results of H. S. Taylor and Sickman[2] for the adsorption of hydrogen on zinc oxide serve as an example of this phenomenon and are presented in Table 22. The significance of this observation cannot be decided until data are available for the change in the true energy of activation as saturation of the surface proceeds. Even if it is then found that a gradual increase occurs, this may not be caused by any inherent difference in the quality of the active centres but may be due to a steric effect. The

---

[1] *J.A.C.S.*, 1934, 56, 642.

[2] Ibid., 1932, 54, 602.

relation between true and apparent energies of activation is discussed on p. 163.

TABLE 22

Adsorption of hydrogen on zinc oxide

Amount adsorbed *c c.*	*Apparent activation energy, K-cals.*		
	110–132°	*132–184°*	*184–218°*
3·0	7·6	7·0	3·8
3·5	9·0	7·5	8·0
4·0	13·2	9·5	10·5
4·5	14·4	11·4	10·7
5·0	15·4	12·7	10·5
5·5	16·0	13·4	10·0
6·0	15·9	14·0	10·3
6·5		14·4	10·3
7·0	..	14·4	10·9
7·5	.	14·7	11·0
8·0	..	..	11·2
8·5	..	..	11·1
9·0	..	.	11·1

The theory of adlineation.

A modified view concerning the location of activity in the catalyst has been expressed by Schwab and Pietsch,[1] in which the active centres of Taylor's theory are replaced by phase boundaries. This means that reaction will occur mainly on a series of lines in the catalyst, so that the term 'adlineation' has been applied to the theory.

There is ample experimental evidence for the preferential adsorption of ions on crystal edges, as illustrated by the phenomena of crystal growth in mixed solutions and by the colouring of different faces of a crystal growing in liquids containing mixtures of dyes. Pietsch, Kotowski, and Berend[2] have also demonstrated the fact that reactions on crystal surfaces occur at linear discontinuities of the solid; this point is illustrated by microscopic examination of such changes as that between crystals of hydrated copper sulphate and hydrogen sulphide, or between solid nickel sulphate and dimethyl glyoxime. Such examples are not, perhaps, strictly

---

[1] *Z phys. Chem*, 1928, 1 B, 385, 1929, 2 B, 262, *Z. Elektrochem.*, 1929, 35, 573, *Katalyse*, by G M. Schwab, 1931.

[2] *Z. phys. Chem.*, 1929, 5 B, 1.

comparable with that of a gas in contact with a catalyst, but illustrate the point in a qualitative manner.

Schwab has also carried out extensive calculations as to the results to be expected on the assumption that molecular impingement on a linear part of a catalyst is the significant factor in determining the kinetics of a heterogeneous reaction, and has shown that this method of treatment leads to equations in good agreement with experimental data, under conditions with or without retardation from the reaction products. Maxted[1] further considers that his observations on the linear effect of poisons on catalyst activity are compatible with Schwab's adlineation theory, as the active parts of the catalyst would, under the conditions postulated, be very similar among themselves although differing largely from the relatively inert bulk of the material.

Additional support to the theory is given by a number of results of Hüttig (pp. 172–6) with reference to the behaviour of mixed oxide catalysts, in which increased catalytic activity was shown to coincide with incipient appearance of a new phase.

Promoter action.

When the effect of promoters is considered in the light of the two alternative theories, rather different points appear to be of importance. In the case of active centres the promoter may be expected to function either by increasing the number of these, or by preventing their coalescence and consequent loss of activity. The former possibility is excluded by the results obtained in the study of carrier action (p. 91) where it was shown that a promoted catalyst contained fewer active patches than the unpromoted catalyst. This fact receives further support from calculations on the number of active centres concerned in the activated adsorption of hydrogen by promoted molybdenum catalysts, which are described in detail in Chapter VII.

There is also direct evidence that a promoter may function by preventing the growth of large crystals, as in the case of iron-alumina catalysts used for ammonia synthesis, but under

---

[1] *J.C.S.*, 1934, 26.

these circumstances no alteration in the quality of the active centres should be involved. It is not yet possible to decide whether this is the case or not, but it seems necessary to conclude that two distinct types of promoter action must exist if active centres are responsible for catalytic effects. In one of these the promoter functions by creating a new type of active centre where the energy of activation is materially lower than is the case with the simple catalyst. In the other it plays its part merely by preserving an existing point of high activity. Both these possibilities are quite different from compound formation.

The action of promoters on the basis of the adlineation theory would be due to an increase in interphase boundaries on the addition of the second component; this is equivalent to an increase in the active area of the surface, which has already been proved not to occur. If, on the other hand, the optimum quantity of promoter were determined by its solubility in the main catalyst, there might be a decrease in the number of active centres simultaneously with a change in their quality.

The fact that the optimum concentration of a promoter element is independent of the chemical character of the latter, but only dependent on the catalyst itself, may at first appear to disprove the suggestion of solubility being involved, as the solvent power of one oxide for another will certainly vary with the nature of the solute. But if the expression 'solubility' in this connexion is taken to mean the capacity for actual entry into the crystal lattice, the results, over the very small concentration ranges involved, would be independent of the particular element employed.

It is also significant that the optimum promoter concentration varies with the reaction in which the catalyst is used, as exemplified by the case of molybdenum oxide for decomposition of hydrocarbons at 500°, and for deoxidation of phenol at 450°. On the other hand, the adsorption data for a series of hydrocarbons on molybdenum oxide catalysts (p. 40) show that the concentration of promoter required to give the maximum effect was the same in each case.

The evidence of Huttig, previously mentioned, cannot be considered as applying to cases of promoter action proper, as it certainly relates to compound formation. The suggestions of Balandin and Rubinstein[1] concerning mixtures of nickel and alumina used for simultaneous dehydration and dehydrogenation of iso-amyl alcohol, and subsequent decomposition of valeric aldehyde, also cannot apply to promoter action. The catalysts contained the components in equal amounts, and were prepared by precipitation under varying conditions. It was found that the energies of activation for the dehydrogenation altered from 8,850 to 22,400 calories, for the dehydration from 17,950 to 45,100 calories, and for the aldehyde decomposition from 14,500 to 33,100 calories, the ratio of the three values being roughly constant for any particular catalyst. It was concluded that the dehydrogenation reaction took place on the nickel surface and dehydration on alumina, but the only place where a constant relation could exist between the two was at the interface nickel-alumina.

It is evident that these conditions are quite different from real promoter action, as with the latter the second component may be completely inactive catalytically.

These considerations may be summarized as follows: mixed catalysts show increased activity on account of three distinct causes. (1) Interaction between the two components leads to the separation of a new phase with a higher activity. (2) The growth of crystals of the active catalyst is prevented by admixture of an inert material with it. (3) Promoter action takes place by the creation of a new type of active centre, but by a mechanism quite different from compound formation.

It is also possible to imagine that different parts of a simple catalyst surface should have specific effects, as even perfect crystals will develop Smekal cracks owing to unbalanced surface forces. As every shade of difference between the conditions postulated by Taylor's theory and the idea of adlineation appears to exist, there is no necessity to decide which of the two is preferable.

The catalytic decomposition of ozone.

When ozone comes into contact with silver oxide it is decomposed. This process, which was investigated by Strutt,[2]

---

[1] *J.A.C.S.*, 1935, 57, 1143.

[2] *P.R.S.*, 1912, 87 A, 302.

offers the remarkable case in which every collision of the reacting molecule with the catalyst was found to be effective. It must, therefore, be presumed equally that every portion of the catalyst surface is active.

The state of the molecule on the catalyst surface.

A more precise description of the state of individual molecules on the surface of a catalyst has been attempted by a few investigators, among whom Burk and Balandin may be mentioned.

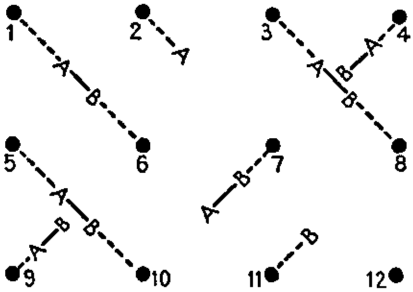


FIG. 76. Diagram of catalyst surface.

Burk[1] postulated that, for a molecule AB to be activated so that it could undergo decomposition, both parts must be simultaneously attached to the surface so that a certain amount of strain was set up. In the diagram representing part of a catalyst (Fig. 76) containing twelve active points which are numbered, and which may or may not be of uniform character, the alternative methods of adsorption of the molecule or of reaction products A and B are illustrated. The molecule held by means of a single link attached to the A or B part of the molecule alone is not in a state to undergo decomposition, and it is emphasized that pairs of active spots which are to act simultaneously must be very close to each other in order to share a single molecule.

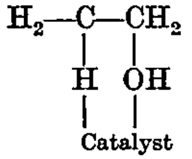
Experimental support of these views is very difficult to find, and one of Burk's strongest arguments was based on the observation that the presence of a poison on a catalyst did not reduce the adsorption of a reactant at the same time as

[1] *J. Phys. Chem.*, 1926, 30, 1134.

it lowered the activity. Such measurements, however, were made at ordinary temperatures, and no information is yet available as to the effect of poisons on activated adsorption at higher temperatures.

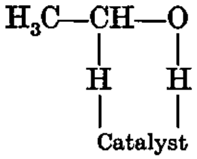
Balandin has applied similar assumptions to a more extensive treatment of the subject in a series of papers.[1] He assumes that fission of a molecule will occur when it is simultaneously held on more than one part of the surface, and that combination will take place when two atoms or radicals are simultaneously adsorbed on a single active centre. In the case of alternative methods of decomposition of a molecule such as alcohol, the course followed will depend on the particular portion of the molecule which is actually held. Dehydration, for instance, will take place under the conditions represented by diagram (*a*) below, while the production of an aldehyde and hydrogen will result from the alternative (*b*).

(*a*)



$$H_2-\underset{\substack{|\\ H\\ |}}{C}-\underset{\substack{|\\ OH\\ |}}{CH_2}$$

(*b*)



$$H_3C-\underset{\substack{|\\ H\\ |}}{CH}-\underset{\substack{|\\ H\\ |}}{O}$$

The presence of more than one type of active centre in a catalyst is accordingly more likely to give rise to decompositions, and the qualitative effects of promoter action may be thus explained.

In a further discussion of his multiplet theory Balandin has considered the case of dehydrogenation of cyclohexane. This is known to occur on platinum which has the face-centred cubic structure represented by the diagram in Fig. 77, and on which the cyclohexane molecules can be accommodated as shown by simultaneous adsorption at a number of different points. As a consequence, the six hydrogen atoms will be split off simultaneously in pairs, and only a face-centred cubic surface having lattice constants between definite limits will act as a catalyst for this reaction.

The constants deduced are from 1·397 Å and 1·237 Å, which are characteristic of palladium and nickel respectively,

---

[1] *Z. phys. Chem.*, 1927, **126**, 267; 1928, **2 B**, 289.

and Balandin has found that this classification does actually hold good for the surfaces which are active in decomposing cyclohexane. But there are grave objections to the general adoption of this picture. The mere fact that no intermediate stages, such as di- or tetra-hydro benzene, can be isolated from the reaction does not necessarily mean that they are not produced, but only that they may decompose more quickly than the fully hydrogenated ring. It is also difficult to explain why the same type of dehydrogenation is catalysed by a wide range of oxides, as for example, those described on p. 146, or why molybdenum oxide is a useful catalyst in the synthesis of cyclohexane or dekalin by direct hydrogenation under pressure, as well as having a profound influence on the hydrogenation of a very wide range of organic compounds containing oxygen, sulphur, and nitrogen.

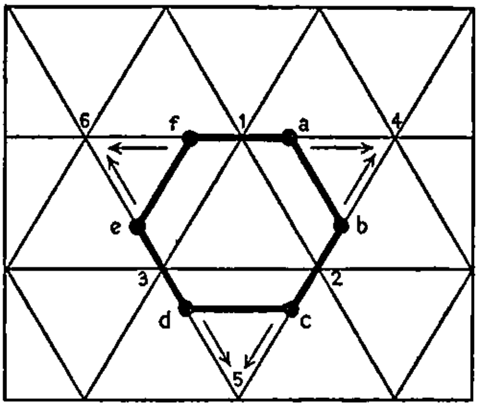


FIG. 77 Adsorbed cyclohexane molecule.

Balandin's general discussion of the effects of affinity between the catalyst and the reactant, however, are in close accord with experimental evidence.[1] He has considered the hydrogenation of the various links C—Cl, N—O, C—O, N—N, C—N, and C—C, and compared the results obtained in the presence of nickel with those to be anticipated on the grounds of affinity between the catalyst and the component of these molecules which is to be split off. There is remarkably good agreement in the two cases, and the ease of fission decreases

---

[1] *Z. phys. Chem.*, 1929, 3 B, 167.

in the order shown above. The similarity between this mechanism and the general ideas concerning activated adsorption is evident.

The case of hydrocarbon adsorption on a wide range of surfaces is of interest in this connexion, and the fact that this may occur without decomposition taking place has already been mentioned (p. 44). There is a further significance in this series of experiments when the gaseous reaction products in different cases are considered, and the data of Table 23 clearly indicate that decomposition reactions of widely varying types may occur with a molecule such as hexane.[1] That these differences are not due merely to the degree of catalyst activity is shown by the fact that hydrogen may be formed in large proportion when the surface is not particularly active, and alternatively may only be present in relatively small amount when very rapid decomposition occurs. This leads to the conclusion that the hydrocarbon molecule must be differently held on specific surfaces, and there is a strong probability that this is due to adsorption on more than one kind of active spot.

TABLE 23

Activity of catalysts for decomposition of hexane at 500°, and the composition of the gaseous products obtained

Catalyst	*Activity*	*Methane*	*Unsaturated hydrocarbons*	*Hydrogen*
Co	4,280	28 6	3 0	68 4
*Ti-Mn oxides	2,250	23 5	5 3	71 2
*Cr-Mn ,,	1,850	28·4	5 5	66 1
*Ti-Al ,,	1,624	23 6	8·9	67 5
Charcoal	1,350	18·4	3 4	78 2
Ti oxide	1,095	36 6	0·6	62 8
Th ,,	486	65 4	11 3	23 3
Al ,,	465	53 0	15 4	31 6
W ,,	336	51·5	15 2	33 3
Zn chromate	330	81 8	6 1	12 1
Ce oxide	326	67·0	9·7	23·3
V ,,	261	82 3	6 2	11 5
Zn tungstate	154	76 1	8·0	15 9

* These contained 1 promoter atom to 10 catalyst atoms.

---

[1] Griffith and Hill, unpublished data.

Additional evidence is provided by the observation that a decane molecule appears to take up more room on the catalyst surface than is required by hexane (p. 88). If the hydrocarbons were adsorbed by their terminal atoms only, there would be little difference between the closeness of the packing. Finally, it has long been appreciated that the effect of a catalyst on a series of different reactions is not proportional to the relative ease with which the uncatalysed changes take place. Further experimental evidence concerning the distance between active spots on the catalyst surface, and their relation to the behaviour of molecules of different sizes, would be of very great assistance in illuminating some of the many difficulties which still remain in this treatment of the subject.

Orientation of adsorbed molecules.

The suggestion has been made by Porter[1] that in an adsorbed layer of molecules the correct arrangement for a reaction with a colliding molecule may arise if there is orientation at the surface, and that such a condition would greatly increase the probability of the change taking place. This idea is a more precise exposition of that put forward by Hinshelwood,[2] to the effect that an adsorbed molecule was held so firmly by the surface that the collision of a second molecule was much more effective. Neither of these suggestions, however, can apply to the case of a single type of molecule which is decomposed on the surface, and it is extremely unlikely that any molecule is rigidly held throughout its length. If Porter's theory were correct, differences in activity should be expected with the odd and even members of a series containing long chains, and X-ray or electron diffraction methods should reveal the arrangement of the molecules on the surface

The data of Germer[3] indicated that electron diffraction methods can in fact show the presence of adsorbed molecules on a surface, but that while these are found to be oriented at low temperatures they are not so when the temperature is raised.

---

[1] *Nature*, 1930, **126**, 349.

[2] *J.C.S.*, 1923, 2729.

[3] *Z. Physik*, 1929, **54**, 408.

Affinity between the catalyst and the reactant.

The decompositions of organic molecules, which have been compared by Balandin (p. 145) when different typical substituent groups were present, is in general agreement with existing ideas regarding the influence of chemical affinity on the adsorption of a reactant. The quantitative treatment of the subject is, however, far from perfect, and it is impossible to draw a sharp line between cases of compound formation and those in which activated adsorption takes place.

Neumann,[1] for example, has established the fact that, when vanadium catalysts are used for the oxidation of sulphur dioxide to trioxide, there is definite compound formation, detectable at 100° and predominating at 500°, with the sulphur dioxide. Similarly, in the case of the ammonia equilibrium in contact with a series of metal catalysts, Frankenburger[2] considers that the reactions

$$M_xN + H \rightleftharpoons M_xNH$$
$$M_xNH + H_2 \rightleftharpoons M_xNH_3 \rightleftharpoons M_x + NH_3$$

are reversible at each stage. The elements which are useful in this connexion are iron, tungsten, molybdenum, and osmium, but they behave very differently with respect to their formation of nitrides, and it is concluded that when compound formation takes place on the catalyst the product must not be too stable. Langmuir's earlier researches on the behaviour of monatomic films of gases on tungsten[3] indicated the same kind of thing. While low pressures of oxygen gave rise to the monatomic layer, an excess of the gas gave WO_3 molecules, which distilled from the metal surface at high temperatures—a process which is used in cleaning up traces of oxygen from a low-pressure system.

The interaction of nitrogen with tungsten or molybdenum was found to be quite different, only volatilized atoms of the metal giving rise to the formation of nitrides. With other gases again, such as ammonia, carbon dioxide, cyanogen, and

---

[1] *Z. Elektrochem.*, 1929, 35, 42; 1934, 40, 764.

[2] Ibid., 1933, 39, 45, 97, 269.

[3] *J.A.C.S.*, 1915, 37, 1139; 1916, 38, 2267.

water, decomposition occurred, while carbon monoxide could produce an adsorbed film.

It may be noted that the comparative rarity of the occurrence of poisoning of oxide and sulphide catalysts is undoubtedly related to their greater stability to chemical attack; that is to say, the phenomenon of poisoning is related to questions of affinity.

The conditions under which a particular part of an organic molecule are activated have been considered by H. S. Taylor, Morikawa, and Benedict[1] They have shown that the behaviour of the C—C and the C—H links in a substance such as ethane can be differentiated by studying the two reactions

$$(1)\quad C_2H_6+mD_2 \rightarrow C_2H_xD_y$$

where $x+y = 6$, and m may be varied,

$$(2)\quad C_2H_6+H_2 \rightarrow 2CH_4$$

in which the C—C link is broken With a nickel catalyst at 138°, reaction (1) took place quantitatively while reaction (2) was negligible, the latter only beginning at 150°.

Similar methods may be applicable to the study of other links in organic molecules.

The behaviour of isomers.

In the case of organic molecules, differences have been observed in the behaviour of isomeric substances when undergoing change in contact with a catalyst. The three cresols, for example, have been found[2] to vary considerably in the ease with which they are converted to toluene by hydrogenation with vanadium oxide as a catalyst. In Table 24 are

TABLE 24

Comparison of different phenols

Phenol	*Per cent hydrolysis* Na *salt at 25°*	*Dissociation const. free phenol, 25°*	*Rate of conversion to hydrocarbon*
Phenol	5·60	$1{\cdot}15\times10^{-10}$	45·8
m-cresol	6·08	0·98 „	43·0
p- „	7·27	0·67 „	32·1
o- „	7·54	0·63 „	22·4

---

[1] Ibid., 1935, 57, 2735.

[2] Griffith, unpublished data.

shown the relative velocities of reaction, together with that of phenol, and the data of Boyd[1] for the corresponding acidities, where it will be seen that there is a parallel between the two

Conversely, the choice of the catalyst may determine the isomer which is formed in a reaction, as shown by the fact that the hydrogenation of naphthalene was found by Willstätter and Seitz[2] to give trans-dekalin when nickel was the catalyst, while if platinum was used the cis-isomer was produced.

Mobility of the adsorbed layer.

The bearing of surface mobility on the question of catalysis is at present ill-defined, but according to H. S. Taylor[3] is not likely to prove of importance, as it is probably only possible in cases of van der Waals adsorption. There is considerable evidence that such mobility exists, from the experiments of Volmer,[4] and that it has a temperature coefficient which indicates a definite energy of activation for the process.

Another example is provided by the experiments of Bosworth,[5] in which the mobility of sodium on a tungsten filament was measured by a photo-electric method. The surface was cleaned from adsorbed material, with the exception of the monatomic film of oxygen, and a beam of sodium ions was fired at a small part of the strip. It was found that sodium was absorbed by the metal up to a point where it appeared as a surface patch; this patch was then observed to decay at a rate depending on the temperature, the strip becoming uniformly active after 1 or 2 hours at 300° K. and after 5 to 10 seconds at 800° K. An example of the distribution curve for sodium over the filament is given in Fig. 78 for determinations at room temperature.

The migration was discovered to have an energy of activation equal to that determined for the adsorption process, and it therefore appeared likely that the latter consisted of migration down slip planes and cracks in the metal crystals.

---

[1] *J C S*, 1915, **107**, 1540.

[2] *Ber.*, 1924, **57**, 683.

[3] *T. Farad Soc.*, 1932, **28**, 135.

[4] *Z Phys. Chem.*, 1925, **115**, 239; 1926, **119**, 46; Moll, ibid, 1928, **136**, 183, &c.

[5] *P.R.S.*, 1935, **150 A**, 58.

For the sake of simplification the material in this chapter has been separated from that which follows, concerning the mechanism of catalysis. The two are so intimately connected with each other, however, that the division of the subjects discussed has been largely of an arbitrary nature, and no intention of segregation is implied by the choice which has been made as to the particular headings under which any of the points are mentioned.

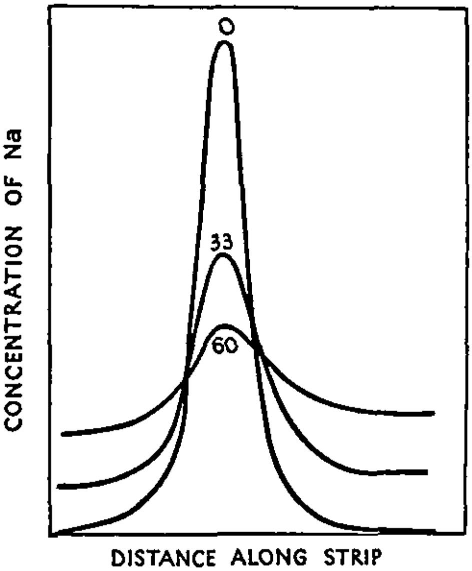


FIG. 78. Migration of sodium on tungsten. Time at room temperature shown in minutes.

CHAPTER VII

THE MECHANISM OF CATALYSIS

In considering the theoretical treatment of catalytic processes by means which have not already been discussed, there are two important subjects which remain. These are the kinetics of heterogeneous reactions, and the energy relations involved in the changes which take place.

Kinetics of catalytic reactions.

Although the simple view that a contact reaction took place by reason of collision effects was considered at an early date, it was quickly realized that such ideas were untenable as a general explanation of catalysis. The fundamental investigations of Langmuir on surface films, and the kinetic studies of Bodenstein and of Hinshelwood have together given a much clearer picture of the mechanism of heterogeneous reactions.

The occurrence of decomposition reactions which may follow alternative courses, such as the production of ethylene and water or hydrogen and acetaldehyde from ethyl alcohol, shows clearly that catalytic effects of this nature cannot be explained on the grounds of collision alone. In the development of the experimental investigation of this subject the most illuminating results have been obtained by comparison of homogeneous and heterogeneous reactions, and by reference to the effects of retardation on the apparent order of a reaction. Only sufficient typical examples will be considered here to provide a brief survey of the possibilities, and for the full treatment of the subject reference should be made to Hinshelwood's book, *The Kinetics of Chemical Change in Gaseous Systems.*

The adsorbed molecule.

Langmuir's ideas as to the nature of adsorption may be applied to the consideration of the simple case in which only a single type of molecule is taking part in the reaction at the surface. If the equilibrium between condensation on, and evaporation from, the surface is supposed to be unaffected by any chemical changes which occur, the velocity of the reaction will be proportional to the m/nth power of the gas pressure, where m is the number of adjacent spaces on the surface which take part in the change, and n spaces are occupied by each molecule.

For example, when hydrogen molecules are dissociated into atoms, the rate is proportional to the square root of the hydrogen pressure; that is, $m/n = 0{\cdot}5$, and the condition on the surface is that a single molecule occupies two spaces. When $m/n = 1$, however, it is not always possible to decide whether the reaction is really unimolecular or whether both m and n have an equal higher value. The order of a reaction may also change as the pressure is increased, becoming independent of pressure once the whole surface is covered with the reactant. A further complication will arise in cases where the reaction product has a retarding influence, and a unimolecular reaction will then appear to be of zero order within certain pressure limits.

Unimolecular reactions.

Examples of simple unimolecular reactions were found by Hinshelwood and Topley[1] in the decomposition of formic acid on glass, platinum, rhodium, and other surfaces. In the decomposition of ammonia Hinshelwood and Burk[2] found that on platinum at 1,000° the reaction was retarded by adsorption of hydrogen and was apparently of zero order, the velocity being inversely proportional to the pressure of added hydrogen. Similar results were obtained by Kunsman[3] for the decomposition of ammonia on tungsten and molybdenum, but at low pressures the reaction tended to become unimolecular; Arnold and Burk[4] also showed that retardation occurred in the decomposition of ammonia by osmium.

In the case of decomposition of nitrous oxide[5] on platinum Hinshelwood found that the reaction appeared to be of zero order on account of retardation by oxygen. If the wire was

---

[1] *J.C S.*, 1924, **125**, 393.

[2] Ibid., 1925, **127**, 1105.

[3] *J.A C S.*, 1928, **50**, 2100.

[4] Ibid., 1932, **54**, 23

[5] *J C.S.*, 1925, *127*, 327.

heated in oxygen it was poisoned, but on reheating *in vacuo* its activity was restored.

In the decomposition of phosphine studied by Melville and Roxburgh[1] the reaction was unimolecular on tungsten at 400–600° and pressures up to 300 mm., while with molybdenum the change became of zero order at the higher pressures.

Finally, the observation of Hinshelwood,[2] that a platinum catalyst which showed practically no retardation of the decomposition of hydriodic acid still exhibited such retardation with ammonia, is of great interest. To summarize the evidence of these experiments with a single type of reacting molecule, it may be concluded that truly unimolecular reactions often occur, but that retardation frequently comes into play. Its appearance will depend on the particular catalyst which is being used, and a surface which exhibits retardation for one reaction will not necessarily do so for a different reaction. There are obviously, therefore, distinct parts of the same catalyst involved in different reactions.

Bimolecular reaction with a single type of molecule.

Some interesting examples of this kind have been described by Hinshelwood and Green,[3] and by Hinshelwood and Allen.[4] In the decomposition of nitric oxide on platinum the reaction was bimolecular, but owing to retardation it appeared to be unimolecular. For the decomposition of acetaldehyde it was found that the activities of platinum, rhodium, gold, or tungsten surfaces were very similar but that the reaction presented some unusual features. At pressures higher than 150 mm. the reaction approached unimolecular conditions but was bimolecular at lower pressures. Now the order of a bimolecular reaction can be reduced from three possible causes:

1. Marked adsorption of the reaction products takes place so that increase in pressure alters the retardation simultaneously with the changes it produces in the rate of reaction.

---

[1] *J C S.*, 1933, 586.

[2] Ibid., 1925, **127**, 2896.

[3] Ibid., 1926, 1709.

[4] *P.R.S.*, 1928, **121** A, 141.

2. The surface is saturated with the reactants so that once this point is reached alteration in the pressure has no effect; this would lead to a reaction of zero order, and an apparent unimolecular stage might conceivably have a very transient existence during the change of order when the saturation of the surface was just incomplete.
3. Reaction occurs between one adsorbed molecule and one free molecule in the gas, probably by direct impact of the latter; as the number of such impacts is directly proportional to the pressure, but the number of adsorbed molecules reaches a saturation value with rise in pressure, the order of reaction will change.

In the case under discussion it was found that the retarding effect *of the decomposition products was far too small to* make the first explanation possible, and the second suggestion also appeared highly improbable, so that there is good evidence for the existence of a case where collision between an unadsorbed and an adsorbed molecule leads to reaction. Further reference to this point will be found on p. 158. The very similar results given by the different types of wire were also associated with a very feeble catalytic effect, and the mean value of the energy of activation for the heterogeneous reaction was actually found to be slightly higher (46,800 cals) than was the case with the homogeneous reaction (45,500 cals.) This suggests that the decomposition was due to a non-specific thermal effect of the hot surfaces, and was closer to surface combustion than to catalysis.

Reactions involving two types of molecule.

The circumstances are obviously more complicated when two types of molecule are involved in the reaction. Both may be adsorbed on the surface to an extent depending on the concentration of the other, or adsorption of only one may be necessary. Retardation may also take place and, as there are likely to be products of more than one type, the possibility of such effects is considerably increased.

Under these conditions it is clearly not desirable to catalogue all the individual examples which have been fully explored, but to select a few of the simpler reactions which will set forth the most interesting features and will indicate the general behaviour of such cases The most straightforward behaviour was shown in the conversion of ethylene into ethane. Rideal[1] found that the rate of hydrogenation of ethylene on nickel was proportional to the hydrogen pressure when ethylene was in excess, and to ethylene pressure when hydrogen was in excess, the ethane produced having no effect. Pease[2] studied the same reaction with a copper catalyst, and found that at 150–250° the same relation held as that described above, but that at lower temperatures the adsorption of ethylene became much more pronounced and the hydrogen pressure was the controlling factor.

More complicated relations exist in other systems, such as that of carbon monoxide and oxygen on platinum,[3] where very strong adsorption of carbon monoxide occurs, and the reaction may proceed either by free molecules of carbon monoxide striking an oxygen molecule adsorbed on one of the few remaining free spaces, or by oxygen being adsorbed on a free space adjacent to adsorbed carbon monoxide. Similar conditions probably exist in the combustion of hydrogen in contact with silver,[4] where very strong oxygen adsorption occurred, or on gold,[5] where further complications due to retardation by water were also recognized. Chapman, Ramsbottom, and Trotman,[6] at an earlier date, had recognized the retardation due to oxygen on silver, and showed that the activity could be restored by heating and evacuating the metal.

The interaction of hydrogen and carbon dioxide may be discussed as a final example. Prichard and Hinshelwood[7] found that in contact with platinum, and with removal of the water formed, the rate of carbon monoxide formation was proportional to the hydrogen pressure if the carbon dioxide was constant. When the hydrogen pressure was constant the rate was initially proportional to the carbon dioxide pressure, but higher quantities of the latter had a pronounced retard-

---

[1] *J.C.S.*, 1922, **121**, 309.

[2] *J.A.C S.*, 1923, **45**, 1196.

[3] Langmuir, *T Farad. Soc* , 1922, **17**, 621.

[4] Benton and Elgin, *J.A.C.S.*, 1926, **48**, 3027.

[5] Ibid., 1927, **49**, 2426.

[6] *P.R.S.*, 1925, **107** A, 92.

[7] *J.C.S.*, 1925, **127**, 806, 1546.

ing effect. This indicates that hydrogen and carbon dioxide are adsorbed on different parts of the surface, and similar observations were made in the case of a tungsten catalyst. The particular technique applied to this reaction is interesting, as it indicates how the experimental conditions can sometimes be selected so as to reduce the possibility of retardation by one of the decomposition products.

The behaviour of reactants on the surface of the catalyst.

The nature of the forces taking part in adsorption has already been shown to vary with the temperature of the surface (p. 27), and the view that some deformation of the reacting molecule was a necessary step in its activation has been suggested by a number of experimenters. H. S. Taylor[1] supposed that in simple molecules such deformation would result in the presence of atoms, and the results of Wolfenden for hydrogen (p. 127) gave some support to this idea. The conclusions of Fryling[2] that the heat of adsorption of hydrogen on active nickel catalysts rose to a maximum, as the amount of gas admitted was increased, because the formation of hydrogen atoms on the most active parts of the surface was an endothermic process, are open to serious objection on both experimental and theoretical grounds. The most conclusive evidence for the existence of hydrogen atoms on a catalyst surface is the effect obtained in the conversion of para- to ortho-hydrogen (p. 50), which must take place by disruption of the molecule.

Generally, however, the nature of activated adsorption—which is primarily concerned in catalysis—appears to follow the simplest lines indicated by the valency forces involved, whether these are primary or covalent linkages. In the decomposition of primary alcohols, for instance, on a copper catalyst, Palmer and Constable[3] found that the rate at a given temperature was independent of the length of the molecule and had the same temperature coefficient in each case. This suggests that the behaviour of the molecule depends on the hydroxyl group in a similar way to that in which spreading

---

[1] *P.R.S.*, 1926, **113 A**, 77.

[2] *J. Phys. Chem.*, 1926, **30**, 818.

[3] *P.R.S.*, 1925, **107 A**, 255; **108 A**, 355.

of fatty acids on water depends on the carboxyl group. The fact that the reaction with isopropyl alcohol was much faster indicates that different affinity forces are at work in the latter molecule, which is known, of course, to be different in shape from the primary alcohols.

Simultaneous adsorption of both reactants.

In reactions which involve molecules of more than one type it is possible that only one will show activated adsorption at a particular temperature, and it is of great interest to consider what will occur under these conditions. The study of the kinetics of such reactions has already suggested (p. 155) that there is evidence for the conclusion that only one of the reactants need be adsorbed, and the same conclusion has been drawn from the behaviour of ethylene and hydrogen in contact with platinum wire (p 97). In the latter case also Farkas, Farkas, and Rideal[1] obtained additional evidence in the fact that the production of ethane occurred equally rapidly with hydrogen and with deuterium at low temperatures when the catalyst surface was known to be largely covered with ethylene. At higher temperatures, when activated adsorption of both forms of hydrogen took place, the velocity of reaction was different with H_2 and D_2. These facts can only be explained if the formation of the saturated hydrocarbon occurs at low temperatures by the collision of either hydrogen or deuterium molecules with adsorbed ethylene molecules, no activated adsorption of the former being necessary.

Some direct measurements of the adsorption of sulphur dioxide and carbon disulphide provide further evidence of the same kind.[2] The reaction

$$SO_2+CS_2 = CO_2+3S$$

has been found to occur at about 200° and upwards in contact with titanium sulphide as the catalyst, the effect of temperature being shown in Fig. 79 for a particular set of conditions. When the adsorption of the two reactants was determined on the same catalyst, the isobars of Figs. 80 and 81 were obtained.

---

[1] *P.R.S*, 1934, 146A, 630.

[2] Griffith, unpublished data.

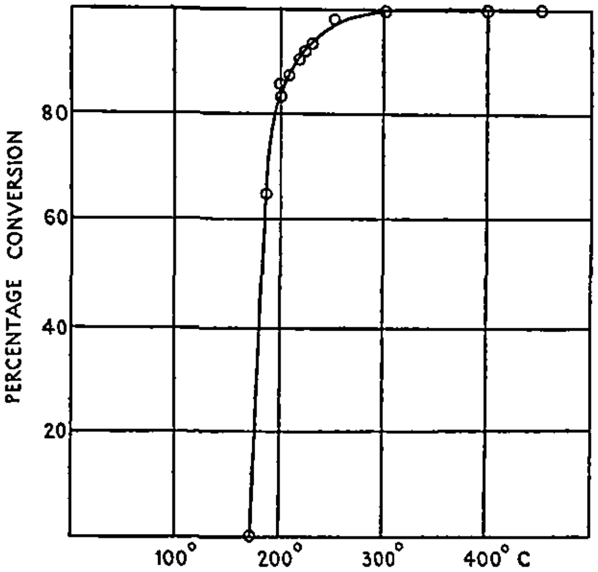


Fig. 79. Activity of titanium sulphide catalyst for conversion of carbon disulphide.
Owing to the very high activity at temperatures above 300° the true values cannot be determined.

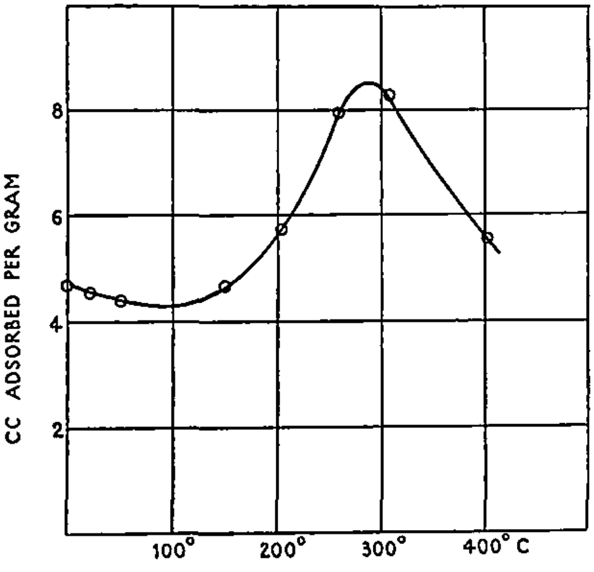


Fig. 80. Isobar for adsorption of sulphur dioxide on titanium sulphide catalyst.

These reveal the interesting fact that no adsorption of carbon disulphide takes place at temperatures where the reaction is measurably fast, but that activated adsorption of the sulphur dioxide is first noticeable in just the same temperature range as that in which the reaction begins. A closer study of the kinetics of this particular reaction, and of the velocities of reaction and sulphur dioxide adsorption, would obviously be of considerable interest.

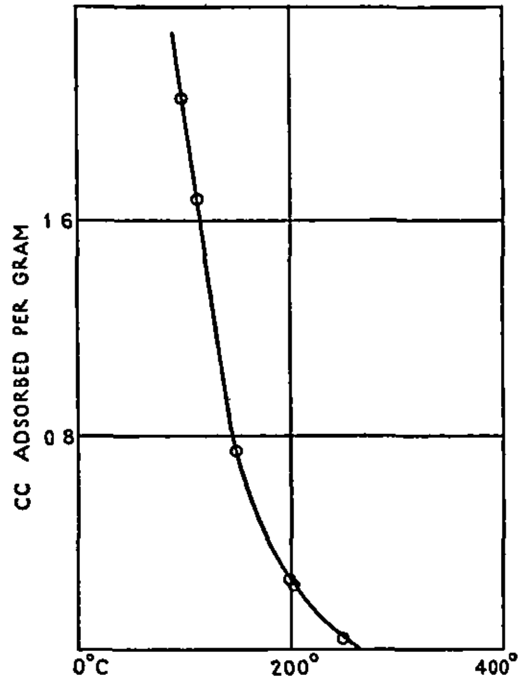


FIG 81. Adsorption of carbon disulphide on titanium sulphide.

The case of activated adsorption is so difficult to separate sharply from that of compound formation, that what has been said concerning the former applies almost equally to the latter. For example, in the synthesis of ammonia by means of iron catalysts, iron nitride can be isolated from the contact mass,[1] and it is evident that under such circumstances the reaction may occur either by activated adsorption of the

---

[1] Applebey, *P.R.S.*, 1930, 127A, 255.

second molecule, or by direct interaction with the compound already formed.

When activated adsorption occurs, the relative velocities of alternative methods of holding the molecule will determine the predominating direction followed by the reaction, as in the case of alcohol decomposition. The final steps in a process of dehydration will be the same as those taking place in activated desorption of water, and with a dehydrogenation reaction similarly the desorption of hydrogen molecules must be involved. A catalyst which exhibits pronounced dehydrating properties should, therefore, be characterized by showing activated adsorption of water at temperatures considerably below that where activated adsorption of hydrogen takes place on the same substance; this has been demonstrated by Taylor and Gould[1] in the case of alumina.

The desorption step will take place rather more slowly than the adsorption, and will require a higher temperature to reach the same velocity. The activation energy for the desorption will equal that of adsorption plus the heat of adsorption, and its variation with the quantity of gas taken up will depend on the relative magnitude of the energy of activation and the heat of adsorption, as well as on their variation with saturation of the surface.

It is therefore important to know the energy of activation for a reaction, for the adsorption of the reactants, and for the desorption of the products in order to gain a complete picture of the process as a whole. It will then be possible to determine which step really controls the velocity of the reaction. Such complete studies have not yet been carried out, but there are cases where the experimental difficulties do not appear to be insuperable. More detailed investigation of a few simple reactions of this type would amply repay the efforts required.

Energy relations in catalysed reactions.

Comparison between heterogeneous and homogeneous reactions is at present only possible in a limited number of cases, but where such data are available it is found that the

---

[1] *J.A.C.S.*, 1934, **56**, 1685.

energy of activation for the catalysed process may be materially lower than that required in the homogeneous phase. Hinshelwood[1] gives the following figures for unimolecular heterogeneous and the bimolecular homogeneous reactions (Table 25). This decrease in activation energy is associated with a total change for two molecules in the one case and for one molecule in the other. The imaginary value for the unimolecular homogeneous reaction can be obtained by calculation, as in the case of hydriodic acid, for example, which was found to give a value of 66·5 K-cals.

TABLE 25

Comparison of homogeneous and heterogeneous reactions

Reaction	*Homogeneous activation energy*	*Heterogeneous activation energy*
HI on gold . .	44 K-cals.	25 K-cals.
N_2O ,, . .	58 5 ,,	29 ,,
N_2O on platinum .	58 5 ,,	32 5 ,,
NH_3 on tungsten .	78 ,,	39 ,,

It has also been observed in industrial application of the synthesis of ammonia that the total energy requirements of the contact process are about one-quarter of that necessary to cause the combination of nitrogen and hydrogen electrically.[2]

The effect of promoters on the energy of activation for the reaction has not been extensively studied, and the evidence available is at present rather conflicting. According to Kunsman[3] the value is not appreciably altered by the presence of promoters or poisons when ammonia is decomposed by iron catalysts, suggesting that the active parts of the surface are not altered in quality but only in quantity. On the other hand Eckell[4] found that when carbon monoxide was oxidized in contact with iron oxide-alumina mixtures, the energy of activation decreased as the alumina content increased, up to the miscibility gap with 25 per cent. of Al_2O_3, but simultaneous changes in the particle size and in the crystal lattice constant were observed (see Fig. 71).

---

[1] *Kinetics of Chemical Change in Gaseous Systems.*

[2] Applebey, *P.R S* , 1930, **127** A, 255.

[3] *Science*, 1927, **65**, 527.

[4] *Z. Elektrochem.*, 1933, **39**, 807, 855.

It is clear that more extensive experiments along these lines would be of great value in elucidating the mechanism of promoter action, and the limited amount of information which is already available will be discussed after a further theoretical treatment of the subject.

Relation between catalyst activity and the energy of activation.

It has been pointed out that adsorption of the reacting molecules on the surface of the catalyst is not alone sufficient to bring about chemical change, but that activation of the reactant must also occur; this activation is, however, restricted to the adsorbed molecules.

Any relation which may exist between the energy of activation of a reaction, and the velocity with which it will take place in contact with a catalyst, must be sought when the velocity constant is stated in terms of the number of adsorbed molecules, and not of the total number in the system. Thus if K is the observed velocity constant and a is the fraction of the total gas which is adsorbed, the true velocity constant x is given by the relation

$$x = K/a.$$

The Arrhenius equation will then apply to the surface reaction in the form

$$d \log x/dT = Q/RT^2,$$

where Q is the true heat of activation. This will only be equal to the observed heat of activation E when the surface is completely covered by the reactant over the temperature range explored, and when no retardation occurs. Hinshelwood[1] has shown that, under more normal conditions with an unretarded reaction involving a single type of molecule,

$$E = Q - \lambda,$$

where λ is the heat of adsorption; and in the case where retardation also occurs

$$E = Q - \lambda + \lambda',$$

where λ' is the heat of adsorption of the retarding molecule,

---

[1] *Kinetics of Chemical Change in Gaseous Systems.*

and when the velocities of adsorption and desorption are much greater than that of reaction. In view of the fact that activated adsorption is now known to have a relatively small velocity, which may be of the same order as that of a reaction, the strict applicability of the above equation becomes doubtful.

There should accordingly be a direct relation between the true energy of activation and the velocity of change, depending on the number of molecules adsorbed on each surface, and thus having a specific factor for different catalysts. The obvious simple case for investigation is where a unimolecular reaction is unretarded by the products on a number of surfaces where the relative degree of adsorption is known. That very large differences in reaction velocity may not accompany equivalent changes in the activation energy is shown by the case of the decomposition of formic acid given in Table 26,

TABLE 26

Decomposition of formic acid

Catalyst	*E*	*Relative velocity*
Glass . . .	24,500 cals.	0 05
Gold . . .	23,500 „	2
Silver . .	31,000 „	2
Platinum . .	22,000 „	100
Rhodium . .	25,000 „	500

but nothing was known concerning the active areas of these surfaces. The need for accurate measurements of heats of adsorption, before calculations of this kind are worth making, is also evident.

Maxted and Moon[1] have pointed out that the simpler Arrhenius equation may be modified to include terms for the heat of adsorption, and may then account for the observation that in certain cases the rate of a catalysed reaction rises to a maximum as the temperature is increased, and then falls again. Zur Strassen[2] studied the hydrogenation of ethylene on a nickel catalyst in the temperature range −10° to 130°, while Maxted investigated the hydrogenation of crotonic and

[1] *J C.S.*, 1935, 1190.

[2] *Z phys. Chem.*, 1934, **169**, 81.

maleic acids with a platinum catalyst; their combined results are shown in Fig. 82. Zur Strassen also found that the rate depended on the hydrogen pressure, and at lower temperatures was independent of the ethylene pressure but nearly directly proportional to ethylene pressure at higher temperatures. There are accordingly the opposing effects of substantial saturation of the surface with ethylene at low temperatures and an increasing dependence on the ethylene adsorption at higher temperatures.

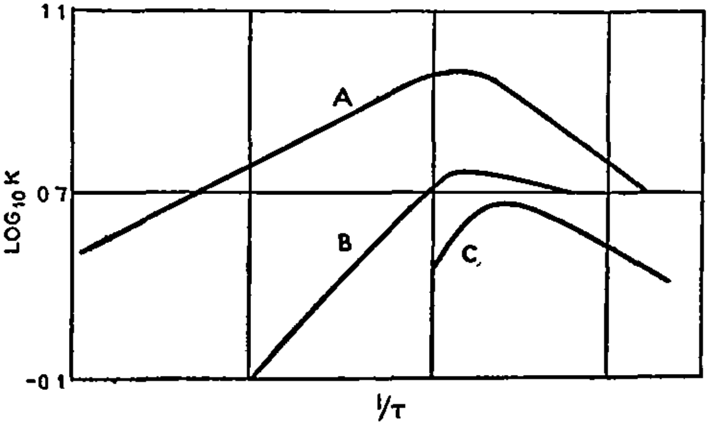


Fig 82. Variation of $\log_{10} K$ with $1/T$
A, ethylene.
B, maleic acid.
C, crotonic acid.

In the modified integrated Arrhenius equation

$$K = ae^{-\frac{[(E-Q_H)-Q_{C_2H_4}]}{RT}},$$

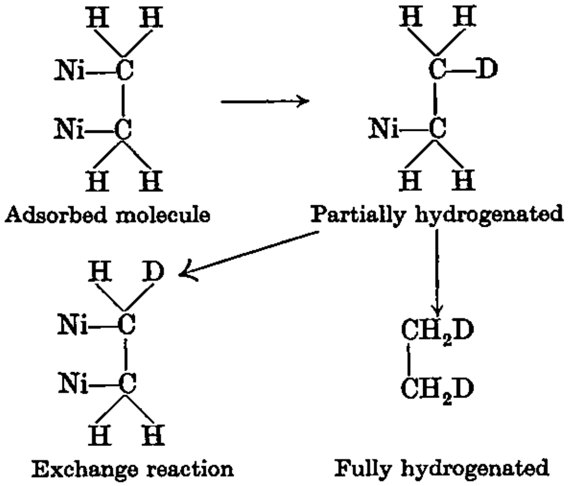
where
K = velocity constant,
E = activation energy of the reaction,
Q_H, $Q_{C_2H_4}$ = heats of adsorption of gases,
a = a factor involving the concentration of the adsorbed gases,

Below the temperature of maximum activity the $Q_{C_2H_4}$ term becomes ineffective owing to the excessive adsorption, and Q_H is less than E so that there is a positive temperature coefficient. When the ethylene adsorption becomes a controlling factor, however, $Q_{C_2H_4}$ is appreciable and the temperature coefficient is negative.

The fact that the curves in all three cases are linear on each side of the maximum supports this argument, but the point could be finally tested by determination of the heat of adsorption of ethylene, or the unsaturated acids, on the catalysts, as this should agree with the value calculated from the difference in slope of the two parts of the curves. Experimental evidence on these lines is not yet available.

Hydrogenation of ethylene.

More detailed investigation of this reaction has shown, however, that it is far from being the simple process which it appeared at first sight. Horiuti and Polanyi[1] found that both exchange and partial or complete hydrogenation of ethylene could occur on a nickel catalyst, as illustrated by the following diagrams for the effect of deuterium on the hydrocarbon:



Hydrogenation would result from the independent approach of two H atoms, and would be bimolecular, while the replacement would be unimolecular with respect to hydrogen; at low pressures, therefore, the latter would predominate, and the exchange reaction would have a lower energy of activation.

---

[1] *Nature*, 1934, **134**, 377; *T. Farad. Soc.*, 1934, **30**, 1164.

Klar[1] also studied the effect of hydrogen and deuterium on ethylene in contact with an iron catalyst at temperatures from 0° to 175°. The reaction with D_2 was slower below 100° but more rapid at the higher temperature, a maximum velocity for H_2 being observed at 125° and for D_2 at 150°; the energy of activation for D_2 was at first lower, and later higher than that for H_2. It was found that the reaction took place at low temperatures with activation of H_2 or D_2 only, but that at higher temperatures activation of the ethylene also occurred; the slower adsorption of D_2 gave rise to the smaller velocity of the change at lower temperatures, but the order of the reaction altered as the temperature was raised.

Tucholski and Rideal[2] studied the reduction of ethylene by hydrogen and deuterium in contact with a nickel wire, which was heated to 200° in the appropriate gas and evacuated before being used in any experiment. It was found that an inversion of temperature coefficient occurred, as previously described, and that the reaction was more rapid with hydrogen than with deuterium below this point.

The difference in the energy of activation was 0·79 K-cals. between 0° and 20°, and 0·5 K-cals. up to 140°, and it is suggested that the former value is in good agreement with the value given by Eyring and Sherman[3] for the difference in the zero-point energy of NiH and NiD.[4] It is argued that the low-temperature reaction is, therefore, controlled by the rate of activation of the adsorbed gas in the form of hydride or deuteride, but that in the higher temperature range, where there is no difference between the rates with the two isotopes, the velocity must be controlled by a factor which does not involve the zero-point energy. It has been found by Melville and Rideal[5] that activated diffusion of H_2 and D_2 into a metal takes place with identical energies of activation, and such a process might limit the rate of reaction for both isotopes. At the same time it must be noted that Klar's observations do not fall into line with this suggestion, and there still

---

[1] *Z. phys. Chem.*, 1935, **174**, 1.

[2] *J.C.S.*, 1935, 1701.

[3] *J Chem Phys.*, 1933, **1**, 345.

[4] Further reference to the zero-point energy is made in a later paragraph, p 169.

[5] *P.R.S.*, 1935, **153** A, 89.

remains the possibility that an exchange reaction is involved which determines the velocity at the higher temperatures. Pease and Wheeler's[1] experiments on the reduction of ethylene by hydrogen or deuterium on a copper catalyst showed that the ratio of velocities decreased from $H_2/D_2 = 1{\cdot}59$ at 0° to 1·04 at 306°, and suggested that the change was due to the increasing importance of the exchange reaction at the higher temperatures.

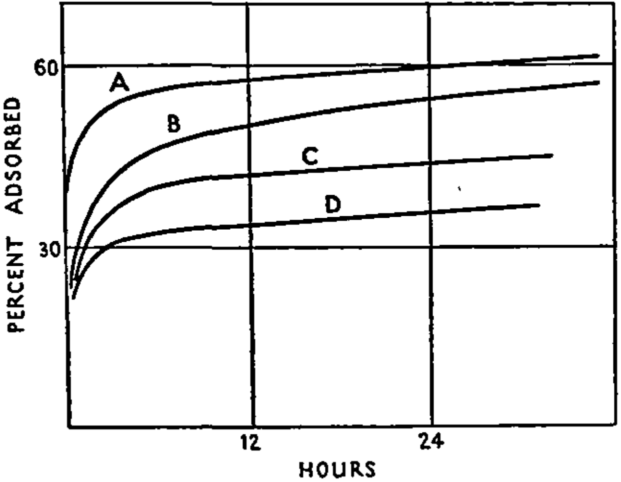


FIG. 83. Velocity of adsorption of hydrogen and deuterium on copper at 0° and 100°

A, hydrogen at 0°.
B, deuterium at 0°.
C, " " 100°.
D, hydrogen " 100°.

Beebe, Low, Wildner, and Goldwasser[2] investigated the adsorption of hydrogen and deuterium on copper at low pressures, and obtained results which have some bearing on this subject. At —78° the differences between the isotopes were only in the rate and not the amount of adsorption, but at 0° and 100° the quantities also were different, as shown in Fig. 83, where it is revealed that less D_2 at 0° but more D_2 at 100° was taken up. Such a temperature inversion would account for the results described by Klar.

---

[1] *J.A.C.S.*, 1935, 57, 1144.

[2] Ibid , 57, 2527.

Energy relations in reactions involving hydrogen and deuterium.

In considering the behaviour of these two isotopes Eyring and Polanyi[1] showed that a difference in the zero-point energy of H_2 and D_2 would amount to 1·7 K-cals., and this should be reflected in a difference in the energy of activation for reactions involving these molecules. Melville[2] has carried out experiments in order to search for this difference, by studying the interaction of carbon monoxide, nitrous oxide, and oxygen, with hydrogen and deuterium. Some of the results obtained are shown in Table 27. The difference in the energy of activation is therefore only about half that anticipated. However, Eyring and Sherman[3] have calculated that the difference will be less when the hydrogen and deuterium are combined with a metal; with NiH and NiD, for instance, the difference is about half that for the free gases. Melville's results, therefore, agree well with the assumption that the zero-point energy plays a part in the energy of activation of a reaction.

TABLE 27

Comparative data for hydrogen and deuterium

Reaction	*Per cent.* D_2	*Temperature*	*Ratio of rates,* H/D	*Difference in energy of activation*
H_2+N_2O	30	192°	2 10	0 69
	30	159°	2 44	0 75
H_2+O_2	30	226°	1 80	0 59
	30	226°	2 09	0 74
	66	177°	2 42	0 78
	66	255°	2 31	0 88

The activity coefficient of a catalyst.

It has already been indicated that a relation should be expected between the energy of activation of a catalytic reaction and its velocity when consideration is paid to the extent of adsorption on the surface. In the integrated Arrhenius equation

$$K = ae^{-Q/RT},$$

---

[1] *Z phys. Chem.*, 1931, **12** B, 279.

[2] *J.C S.*, 1934, 797.

[3] *J. Chem. Phys.*, 1933, **1**, 348.

where K is the velocity constant, the term a has been called the coefficient of intrinsic catalyst activity.[1] Storch[2] has reviewed the information which is available as experimental evidence along these lines.

The results obtained by Balandin for the dehydrogenation of a wide range of organic compounds on different catalysts were apparently confined to reactions of the first order, where the effect of heats of adsorption on the true activation energy were not known. The data of Eckell on the oxidation of carbon monoxide by mixed iron oxide-alumina catalysts mentioned on p. 122 are open to objection on account of possible complications caused by the occurrence of the water-gas reaction by means of adsorbed water, which may also have been present on the catalyst. Storch considers that the data of Constable[3] first indicated the relationship between catalyst activity and the activation energy. In the case of the dehydrogenation of ethyl alcohol in contact with copper catalysts reduced at different temperatures, shown in Table 28, the coefficient a is expressed as the number of molecules held by the surface per second per gramme of catalyst. There is thus a linear relation between $\log_{10} a$ and E.

TABLE 28

Decomposition of ethyl alcohol on copper catalysts

Temperature of reduction of catalyst	*E, K-cals.*	*$\log_{10} a$*
225°	25·61	28·59
235°	25·03	28·51
257°	23·89	27·93
266°	22·07	27·20
275°	21·61	27·15
350°	21·59	26·87

In attempting to explain this relation it is necessary to consider the mechanism of energy exchange between catalyst and reactant rather more closely. The frequency of energy

---

[1] Schwab, *Z phys. Chem.*, 1929, **5** B, 406; 1930, **9** B, 265; Balandin, ibid., 1932, **19** B, 451; Eckell, *Z. Elektrochem.*, 1933, **39**, 859; Cremer, *Z. phys. Chem.*, 1929, **144**, 231.

[2] *J.A.C.S.*, 1935, **57**, 1395.

[3] *P.R.S.*, 1925, **108** A, 355.

transfer Z will be related to the number of active centres in the surface S and the activity coefficient a expressed in molecules per second by the relation

$$SZ = a$$

in the simplest case over a small range of temperature. From the data of Dohse for the dehydration of alcohols on bauxite, numerical values can be assigned to the above relation, as he has found that the number of active centres is 2×10^{19} per gm. of catalyst. This was determined by varying the alcohol concentration in order to discover the amount which was necessary to give just complete saturation. The remaining data which are required are shown in Table 29. Z accordingly varies from $0{\cdot}4 \times 10^{10}$ to $2{\cdot}0 \times 10^{10}$ exchanges per second.

TABLE 29

Decomposition of alcohols on bauxite

Alcohol	*E, K-cals.*	*log_{10} a*
Propyl . . .	28·5	29·2
Butyl . . .	28·0	29·0
Sec-butyl .	24·0	28·9
Iso-propyl . .	26·8	29·6
Tert-butyl . .	20·0	29·1

Although these results indicate that a is approximately independent of the particular alcohol, the data of Palmer and Constable[1] showed that this did not apply in the case of copper catalysts. In Table 30 the ratio of a for ethyl alcohol to a_x for the other alcohol is shown. The last case is interesting

TABLE 30

Decomposition of alcohols on copper

Alcohol	$log_{10}\left(\frac{a_x}{a}\right)$
Propyl	0
Butyl	0
Iso-butyl . . .	0
Iso-amyl . . .	0·4
Iso-propyl . . .	2·4
Cyclohexanol . .	2·4
Allyl → acrolein .	0
Allyl → propionaldehyde.	−3·5

---

[1] Loc cit

as the ratio for the dehydrogenation reaction is 1, but the change to propionaldehyde is about 3,000 times slower. That this decrease is not caused by the small number of centres which are active for this reaction is indicated by the fact that a sintered catalyst gave a higher ratio of propionaldehyde to acrolein. The variation in a thus appears to depend on simultaneous changes in S and in Z, which may both depend on the particular molecule undergoing reaction.

A similar method of approach has been used by Huttig, Novak-Schreiber, and Kittel[1] in consideration of the changes in catalyst activity of mixed oxides. Magnesium oxide and ferric oxide were heated together at different temperatures and then tested as catalysts for the decomposition of nitrous oxide, the conditions being selected so that extensive decomposition of the gas did not occur. It was found that the percentage decomposition was given by the relation

$$\log_{10} x = -q/T + \log_{10} n,$$

where x was the decomposition of the nitrous oxide, q was the energy of activation, calculated from the temperature coefficient of the catalyst activity, multiplied by the factor for conversion of natural logarithms and for the gas constant R, and n was the factor depending on the particular catalyst used and whose value was to be determined. The above equation is precisely the same in form as that already given (p. 169) by derivation from the Arrhenius equation and, although the numerical values are different in the two cases, there must be a direct proportion between n and a.

Further, the relation between a and the number of active centres has already been pointed out, so that the experiments of Huttig should give an indication of the change in the value of Q, and hence of the quality of the active centres, as well as the number of active centres The curves of Fig. 84 show the observed variation in x with the temperature at which the catalyst had been prepared, and with the temperature at which the nitrous oxide was decomposed. The change in the value of the energy of activation with alteration in the temperature of catalyst preparation is shown in Fig. 85, and

---

[1] *Z phys Chem*, 1934, 171, 83.

Fig. 86 indicates the relation between log *n* and the temperature at which the catalyst was made.

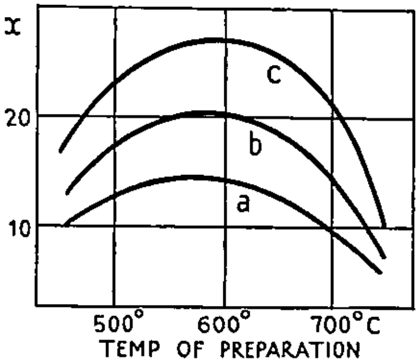


FIG. 84 Effect of temperature of preparation on catalyst activity at different temperatures.

A, tested at 510°
B, „ 520°.
C, „ 530°.

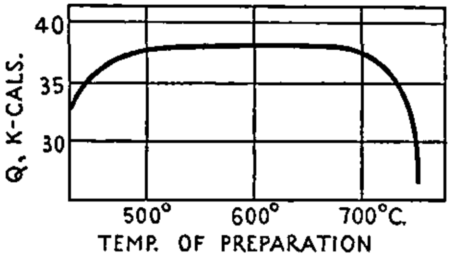


FIG 85. Variation of energy of activation with the temperature at which the catalyst was prepared.

From the character of these curves the following conclusions can be drawn:

1. The nature of the active centres does not alter over a wide range of conditions of catalyst preparation, because the value of the energy of activation remains constant, between 500° and 700°.
2. The number of active centres increases very rapidly in the temperature range 450–550°, and this increase is responsible for the observed change in catalytic activity.

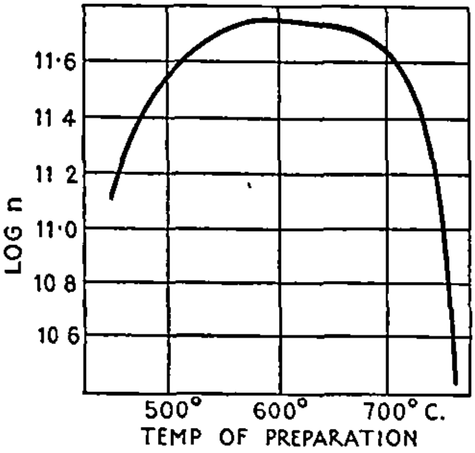


FIG. 86. Variation of log *n* with the temperature at which the catalyst was prepared.

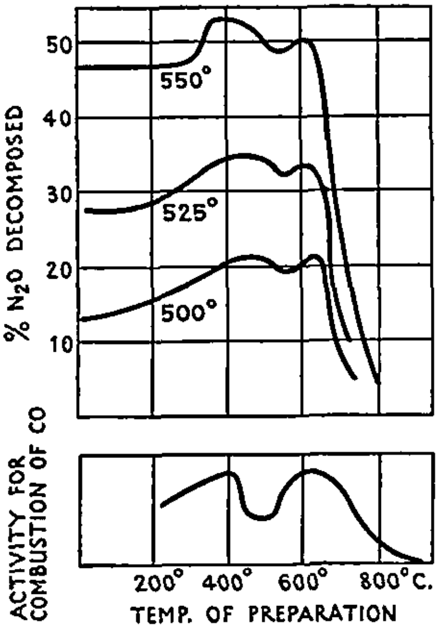


FIG 87. Zinc oxide-ferric oxide catalysts· activity for decomposition of nitrous oxide and for combustion of carbon monoxide, showing the occurrence of two maxima at the same position in each case.

Although this is clearly not an example of promoter action proper, it is of great interest because it shows the application of the method of calculation to a case where compound formation is taking place. The examination of the behaviour of zinc oxide-ferric oxide mixtures by Huttig, Tschakert, and Kittel[1] by similar methods has proved equally interesting.

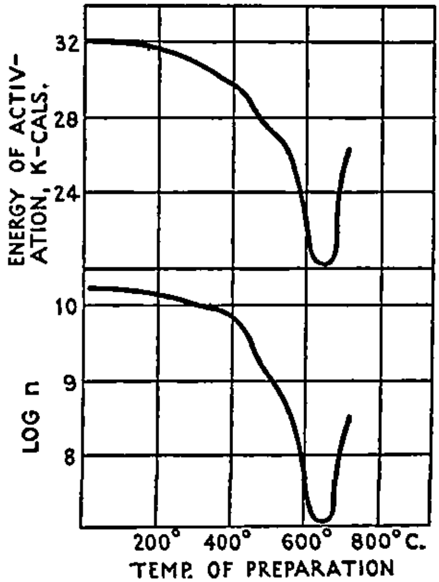


Fig. 88. Zinc oxide-ferric oxide catalysts change in number of active centres and energy of activation for the decomposition of nitrous oxide.

Equimolecular amounts of the two oxides were heated to different temperatures, and the activity of the products for the decomposition of nitrous oxide was determined at three different temperatures. As can be seen in Fig. 87 two positions of maximum activity appeared, and it was found that these coincided with the previously determined maxima for the combustion of carbon monoxide. The reasons for the occurrence of two maxima became apparent on calculation of the energy of activation and of the relative number of active centres; as shown in Fig. 88 the former decreased initially more rapidly than the latter, so that a rise of catalytic effect was produced.

---

[1] *Z. anorg. Chem.*, 1935, **223**, 241.

The position of the second maximum, however, was determined by the incipient formation of zinc ferrite, which was recognized by the appearance of characteristic lines in the Debye pattern and by a sudden increase in the magnetic susceptibility. This offers a further example of increasing catalytic activity at the moment when a new phase first appears but has not become the predominant component.

These two cases indicate the extreme usefulness of this method of investigation, particularly in association with determinations of the physical and chemical properties of catalysts.

Other papers by Huttig,[1] which may be consulted in this connexion, give an extensive summary of a large number of previous contributions on the same subject.

Promoter action and activated adsorption.

The same kind of investigation could be applied to determine the means by which true promoter action increased the activity of a catalyst, if sufficient data were available for an unretarded unimolecular reaction on the simple and on the promoted catalyst. Unfortunately there are not yet experimental data of this kind, although Schwab and Schultes[2] have studied the decomposition of nitrous oxide on a series of simple and mixed catalysts consisting of oxides of copper, zinc, titanium, magnesium, aluminium, iron, and chromium. The mixtures were only prepared by mechanical means, and showed effects of all types, being sometimes additive, sometimes enhanced, and sometimes lowered. But the most active catalysts were associated with a pronounced lowering of activation energy, so that a new type of active centre was clearly being formed. The results at least indicate that the method is extremely promising.

But a clear case can be investigated by use of the facts concerning the activated adsorption of hydrogen on promoted molybdenum oxide catalysts, given by Griffith and Hill.[3] If this adsorption is considered as a unimolecular reaction, which is unretarded and whose velocity is propor-

---

[1] *Z. Elektrochem*, 1935, **41**, 527, *J A.C S.*, 1935, **57**, 2470.

[2] *Z. Phys. Chem.*, 1930, **9B**, 265.

[3] *P.R S.*, 1935, **148A**, 194.

tional to the quantity adsorbed in a given short initial time, the figures of Table 31 can be employed (see also p. 47).

TABLE 31

Adsorption of hydrogen on promoted molybdenum oxide catalysts

Catalyst, Si *atoms to 100* Mo *atoms*	*c.c.* H_2 *adsorbed in 1 minute at 450°, per 100 gm.*	*Observed energy of activation, 400–450°, cals /gm. mol*
0	5·2	29,000
3·0	12·5	23,900
4·4	13·5	23,500
5·5	25·5	17,600
10·0	39·0	16,900

The observed energy of activation must be corrected for the heat of adsorption, which can be calculated from the isobars of Fig. 28. The value of a can then be determined from the equation

$$\log_{10} x = -Q/2{\cdot}3RT + \log_{10} a$$

by inserting the figures shown in Table 32, and it is therefore possible to see how the number of active centres in the catalyst varies with the addition of promoter. These figures show that the addition of promoter actually reduces the number of active centres, but simultaneously alters their quality to such an extent that the catalytic activity is increased. This is confirmation of the conclusion already arrived at during experiments on the behaviour of supported catalysts described in Chapter V.

TABLE 32

Comparison of promoted molybdenum oxide catalysts

Catalyst, Si *atoms to 100* Mo *atoms*	x	Q *corrected*	a
0	5·2	32,000 cals.	$2{\cdot}28 \times 10^{10}$
3·0	12·5	26,900 ,,	$1{\cdot}534 \times 10^{9}$
4·4	13·5	26,300 ,,	$1{\cdot}095 \times 10^{9}$
5·5	25·5	20,900 ,,	$4{\cdot}904 \times 10^{7}$
10·0	39·0	19,700 ,,	$3{\cdot}274 \times 10^{7}$

An extension of this method of investigation, with reference both to adsorption and to different simple reactions, would undoubtedly be of very great interest. At the moment it must be admitted that insufficient information is available concerning the mechanism of activated adsorption, and the relative importance of the individual steps, which must be involved, is not clearly understood.

The picture which is presented by a number of different authors may be summarized as follows: when a molecule of the reactant approaches the catalyst it may be adsorbed, and if the conditions are favourable it will be activated. The next step will be either reaction, or desorption without reaction. There is not yet evidence available as to whether the reaction invariably occurs with the adsorbed molecule or whether it is possible at the moment of desorption. Foresti[1] has carried out careful measurements, by means of thermocouples, during the catalytic hydrogenation of ethylene, and has concluded that reaction is entirely confined to the surface. This observation, however, merely indicates that homogeneous reaction chains are not propagated from the catalyst, and experiments of this type cannot, of course, decide the point. Kobosew and Anochin[2] have shown that a catalyst surface may act as a chain inductor, but such a reaction would, of course, be irreversible in contact with the same surface, thus differing from a true case of heterogeneous catalysis. In the particular case described, the effect of a platinum surface saturated with oxygen on the combination of electrolytic gas was attributed to the formation of hydrogen peroxide, and the ensuing reaction had chain characteristics.

Polanyi[3] supposes that the series of changes involved in a catalytic reaction may be represented by the following equations, for the overall effect $AB+CD = AD+BC$:

$$\begin{aligned}
K- + AB + -K &= KA + BK\\
K- + CD + -K &= KC + DK\\
KA + DK &= K- + AD + -K\\
KC + BK &= K- + BC + -K
\end{aligned}$$

---

[1] *Ateneo Parmense*, 1932, **4**, 401; *Chem. Zentr.*, 1933, i, 1567

[2] *Z. phys. Chem.*, 1931, **13B**, 63.

[3] *J.S.C.I.*, 1935, **59**, 123T.

where $K-$ represents an empty active space on the surface. But a simple picture such as this does not indicate how a decomposition of a single molecule may occur, nor does it specify the proximity which is necessary between separately adsorbed molecules in order that they may react.

The fact that the energy of activation for the dehydrogenation of a series of organic substances was found by Zelinskii and Balandin to be independent of the particular compound but characteristic of the catalyst, suggests that the controlling reaction in some cases may be the recombination and desorption of molecular fragments or of atoms H. S. Taylor and Sickman[1] have pointed out that the desorption of water may well be the rate-controlling factor in the dehydration of organic compounds such as alcohols.

It is therefore evident that information is required not only concerning the energy of activation of the adsorption of the reactants but also for the desorption of the reaction products, so that velocity measurements at different temperatures and determinations of the heat of adsorption are of very great importance. There are possibilities in the direction of determining the order of reaction involved in the processes of activated adsorption, although it is difficult to imagine anything but a unimolecular process of this type. Emphasis may again be laid on the point that the velocity of the different changes involved will have a much greater influence than the total adsorptive capacity of the surface on the course of the reaction. It is obvious that a slow adsorption of which the final stages take days to reach equilibrium cannot possibly be involved in a catalytic reaction taking only a few seconds.

As to the degree of affinity which is desirable between catalyst and reactant, little can be said at the moment; but it seems probable that a very stable link must be considered simply as a case of compound formation, and that under these conditions the original reaction may become so obscured that the kinetics of an entirely different series of changes ought really to be investigated.

---

[1] *J.A C S.*, 1932, 54, 602.

Active centres and energy of activation.

If the energy of activation is to be considered as a criterion of the quality of the active parts of the surface, the existence of centres of varying activity may be determined either by stepwise saturation at low pressures, or by gradual poisoning or sintering of the catalyst. The former method can only deal with one reactant at a time, and has been discussed already; Maxted and Moon[1] have studied the effects of sintering.

They measured the decomposition of hydrogen peroxide and the hydrogenation of crotonic acid, using platinum catalysts which had been deactivated to varying extents by heat treatment. It was found that the ratio of the reaction velocities at two different temperatures did not vary appreciably with the state of deactivation, as indicated by the figures in Table 33 for the decomposition of hydrogen peroxide. These results were taken to indicate uniform activity of all parts of the surface, but no corrections have been introduced for the effect of heats of adsorption on the true values for the energy of activation; it is quite conceivable that the former might alter simultaneously with the latter so that their difference remained approximately constant. It should be of considerable interest to follow changes in the behaviour of a catalyst at much earlier stages in sintering, when the loss of activity of the most active parts should take place.

TABLE 33

Deactivation of platinum catalysts

Temp. of sintering	*Activity per cent original*	$K_{10°}$	$K_{30°}$	*Ratio* $K_{10°}/K_{30°}$
Unsintered	100	0·23	0·634	2·76
250°	23	0·052	0·142	2·73
300°	7·8	0·018	0·050	2·77
350°	4·4	0·0101	0·0275	2·72
400°	2·6	0·00607	0·017	2·80

---

[1] *J.C.S.*, 1935, 393.

Other theories of catalytic action.

Mention must be made in conclusion of attempts which have been made to explain catalysis by hypotheses distinct from any of those which have been already discussed. Nyrop[1] postulates an atmosphere of rapidly moving electrons over a catalyst surface, the effect then depending on the maximum kinetic energy of the free electrons of the catalyst. As a consequence of this assumption it is deduced that adsorbed molecules would react just like gas molecules, and the reaction products formed would be those with highest ionization energy or lowest molecular weight. Promoter action is attributed to an increase in catalyst area, while poisoning, by traces of water, of the iron catalyst used in the synthesis of ammonia, is supposed to be due to the formation of nitric oxide. There are many arguments against these suppositions; for instance, there is no evidence that the adsorbed layer is completely mobile, nor that reaction may occur as a result of van der Waals adsorption alone, and it is known that promoter action is not due to an increase in effective area. Cady and White[2] have also discussed the theory, and pointed out that the kinetic energy of surface electrons should be greater when an alternating current of about 5,000 cycles was passed through a metallic catalyst filament, which should therefore exhibit greater activity. This was investigated with a nickel strip, tested by its effect on the combination of hydrogen and oxygen, but a frequency of 50 kilocycles and currents up to 50 milliamperes gave no evidence of increased activity.

O. Schmidt[3] has suggested that catalytic hydrogenation may take place by two alternative mechanisms. With elements having large atomic volume and small electron expulsion work, such as Cs, Ca, Sr, and Ba, negative hydrogen ions are supposed to be formed, on account of the ease with which free electrons are produced; this is equivalent to the presence of hydrides in which the hydrogen behaves as a positive ion.

---

[1] *Chem. and Ind.*, 1931, 752.

[2] *J. Phys Chem*, 1933, **37**, 823.

[3] *Naturwiss.*, 1933, **21**, 251; *Z. phys Chem.*, 1933, **165**, 133, *Ber*, 1935, **68** B, 1098.

With elements which have a small atomic volume and a large electron expulsion work, on the other hand, the electrons are unstable and hydrogen functions as a positive ion within the crystal cracks, as it cannot exist on the surface. This would occur in the case of copper, chromium, manganese, iron, cobalt, nickel, platinum, and other elements, and hydrogenation would take place in solid solution.

It does not appear likely that this theory would account for many of the phenomena now associated with catalysis, such as activated adsorption, poisoning, and increased effects due to promoter action, and it is also difficult to see how the very similar effects which are often produced by elements and by compounds could be reconciled with such suppositions.

The tunnel theory.

Born and Weisskopf[1] pointed out that, according to quantum mechanics, a possible explanation of the effect of a catalyst was that it allowed penetration of the energy barrier between the initial and final stages of a reaction, this is the so-called 'tunnel' theory. Cremer and Polanyi[2] showed that if this were really the case with a hydrogenation reaction the velocity of the change should be very materially less with deuterium than with hydrogen, and that therefore there should be a concentration of the former in carrying out such a process with a mixture of the two. All attempts to demonstrate such an effect were, however, quite unsuccessful.

No better success attended the efforts of Barrer[3] to demonstrate the reality of the tunnel phenomenon. He found that the ratios of reaction velocities of H_2 and D_2 with carbon varied from 1·44 at 890° Abs. to 2·37 at 500° Abs., and could be completely accounted for by differences in the zero-point energy of the isotopes.

Conclusion.

Although the precise nature of activation is not yet understood, all recent experimental work on catalysis is leading back to ideas closely approaching the old intermediate com-

---

[1] *Z. phys. Chem.*, 1931, **12** B, 206.

[2] Ibid, 1932, **19** B, 443

[3] *T. Farad. Soc.*, 1936, **32**, 481.

pound theory, and is giving stronger support to the view that valency forces are involved in activated adsorption. There appears to be no reason to abandon the concept of active parts of the catalyst having specific adsorptive effects, and it is to be anticipated that the further application of existing methods of study of kinetics and of energy relations is the most promising line to follow in clearing up the various points which are still obscure.

CHAPTER VIII

THE DEVELOPMENT OF CATALYSTS

WHEN the facts presented in the previous chapters are surveyed, the question will naturally be asked, 'Is it possible to predict the best catalyst for a hitherto unexplored reaction?' The answer is that, at the moment, this is not fully possible, and that methods of trial and error are still necessary. But the search may be very considerably shortened by a careful review of all the data available, and will be progressively facilitated as additional information is accumulated.

Catalyst elements and the periodic system.

The selection of a group of catalyst elements may often be made on the basis of the periodic system, as would be anticipated from the gradual transition in chemical properties which is brought out by this classification. A few examples will indicate the extent to which such relations have been found to apply.

1. Oxidation catalysts.[1] In the vapour phase oxidation of toluene by air, complete combustion is produced by cobalt and cerium oxides, while manganese, copper, nickel, chromium, and uranium are rather less active. Vanadium oxide occupies an intermediate position and leads to good yields of benzoic acid, but molybdenum, tungsten, and zirconium oxides give good conversion to benzaldehyde. Most other oxides have very little catalytic action, and the dependence of the effect on the position in the periodic table is apparent.

2. Catalysts for the synthesis of methanol. The active elements in this case are zinc, manganese, chromium, cerium, zirconium, and uranium.[2]

3. The production of sulphur from carbon disulphide. In the interaction of sulphur dioxide and carbon disulphide the relative activity of the various elements is indicated in Fig. 89, tests being carried out under comparable conditions. It is evident that a very close relation exists between the

---

[1] Cf. Marek and Hahn, *Catalytic Oxidation of Organic Compounds*, 1932.

[2] Audibert and Raineau, *Ind. Eng. Chem.*, 1928, **20**, 1105.

position of the catalyst element in the periodic system and the activity of its compound, which was generally a sulphide.[1]

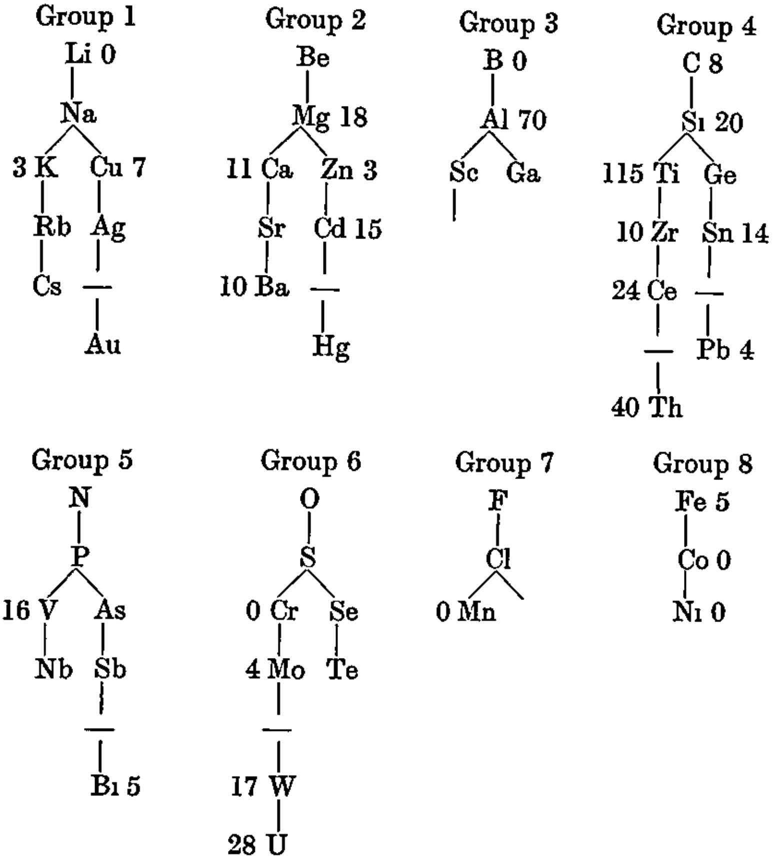


FIG. 89. Part of the Periodic Table of elements.
The relative activity of the elements as catalysts for the interaction of carbon disulphide and sulphur dioxide is shown by the numbers attached to the symbols.

It may also be noted that the relative activity of zirconium would probably fall even more closely into line if it too had been employed as a sulphide, but the oxide which was actually used as the initial material was not converted under the conditions of the experiment.

4. The decomposition of alcohol. Cremer[2] compared the behaviour of alcohol in contact with rare-earth oxides, and

---

[1] Griffith, unpublished data.

[2] *Z. phys. Chem.*, 1929, **144**, 231.

found that the energy of activation of the reaction was indistinguishable in the series Ce, Pr, Nd, Sm, Gd, and Dy, but rose slowly in the group Al, In, Sc, Y, and La.

Activated adsorption and selection of catalysts.

The most useful information concerning an unexplored reaction can be derived from data concerning the adsorption of the individual reactants in the temperature range where the desired equilibrium conditions are known to exist. Thus accumulated facts about the adsorption of a wide range of gases and vapours on surfaces composed of metals, oxides, sulphides, and similar substances, will eventually prove extremely useful in the development of new catalysts.

As an example of this suggestion, the case of the adsorption of hydrogen may be considered. Some figures in this connexion have already been given (pp. 27–33), and a wide survey of other catalysts has been made by Hollings and Griffith,[1] with the results shown in Table 34 and illustrated by

TABLE 34

Adsorption of hydrogen on oxides and metals

c c. adsorbed by 100 gm. of catalyst

	20°	*100°*	*200°*	*300°*	*400°*	*450°*	*P final mm.*
V oxide	33	27	30	490	1,950	1,974	184
Cr „	93	152	280	400	392	385	569
W „	..	3	76	57	38	210†	350
Fe „	24	40	80	360	1,676	1,800	192
Co „	15	613	993	1,014	1,013	1,013	21
Th „	8	7	7	14	67	81	570
Ti „	24	20	17	130	151	156	565
Al „	13	16	20	21	922	1,865	235
*Sn-kaolin	78	68	67	92	268	547	326
*Cd-kaolin	28	33	47	100	185	190	579
Ce oxide	14	12	234	309	334	321	533
Mg „	19	17	21	22	65	65	614
Zr „	7	9	8	31	61	69	516

* These catalysts contained 10 per cent of added china clay in order to prevent fusion of the finely divided metals

† Further reduction appeared to take place at this temperature in spite of previous treatment.

---

[1] *Nature*, 1932, **129**, 834.

the curves of Fig 90. Assuming that activated adsorption of hydrogen proceeds with relatively high velocity in those parts of the isobar where the normal decrease in quantity with rise in temperature takes place, it is possible to draw the following conclusions concerning the use of these substances as hydrogenation catalysts.

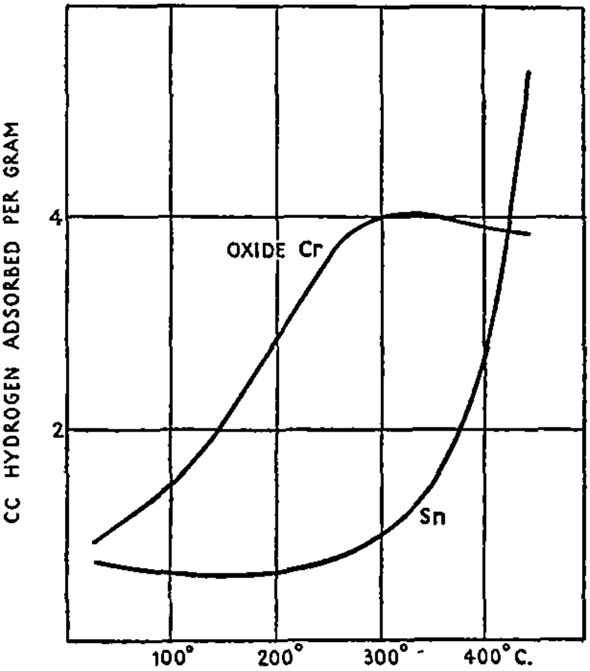


FIG. 90 Two typical isobars for adsorption of hydrogen.

1. The materials fall roughly into two classes: (*a*) those where activated adsorption proceeds with high velocity at relatively low temperatures, as in the case of chromium oxide, (*b*) those in which activated adsorption only begins to become appreciable at the highest temperature explored, as in the case of tin. The isobar for the latter therefore represents conditions of false equilibrium only In the case of cobalt and vanadium the surfaces appear to be practically completely covered with hydrogen over an appreciable range of temperature, thus resembling the behaviour of nickel discovered by Benton and White (see p. 26).

It is accordingly to be anticipated that chromium, vanadium, and cerium should take part in catalytic effects involving hydrogen at about 400–450°, that tungsten should be effective at 50 or 100° lower, cobalt in the neighbourhood of 200°, and nickel even below 100°. On the other hand iron, aluminium oxide, and tin should only be useful above 450°.

These expectations are realized in the known influence of chromium, cerium, and tungsten oxides on the synthesis of methanol from carbon monoxide and hydrogen,[1] of vanadium oxide on the conversion of phenols to hydrocarbons,[2] of cobalt and nickel in the reduction of carbon monoxide to hydrocarbons by the Fischer process,[3] and in the hydrogenation of many organic substances by the method of Sabatier and Senderens. Chromium, vanadium, and titanium compounds are also employed for the formation of hydrogen sulphide and methane by the interaction of carbon disulphide and hydrogen.[4] The use of iron catalysts for the synthesis of ammonia, of tin for the liquefaction of coal,[5] and of the oxides of aluminium and thorium for destructive hydrogenation of hydrocarbons, are also in accord with the same argument.

Such information, however, may only tell half the tale when a reaction involving two types of molecule is considered, but the method can obviously be extended to consideration of each reactant separately. Qualitative data are already available for a range of substances such as hydrogen, oxygen, nitrogen, oxides of carbon, sulphur dioxide, hydrogen sulphide, carbon disulphide, hydrocarbons, and so forth. By gradual compilation of an adsorption register, which recorded the relative velocity with which such compounds were taken up by a wide variety of catalysts at different temperatures, it should not be long before the most likely catalysts, for a reaction involving any pair of the tabulated reactants, could be predicted without recourse to experiment.

The simple position postulated above is, however, complicated by two factors. One of these is the observation that

---

[1] Ger. Pat 293,787, 295,202, &c.

[2] Bruce and Griffith, B.P. 403,708.

[3] *Ber*, 1923, 56, 2428, &c.

[4] B.P. 5291/1878, and unpublished data.

[5] *F.R.B. Annual Report*, 1933, p. 99.

activated adsorption of both reactants does not always appear to be necessary. The other is that retardation or poisoning may take place, but this can be predicted from separate adsorption data. If the velocity and extent of adsorption of reaction products, and of any impurities which are likely to be present in the starting materials, are known, the probability of either poisoning or retardation can be gauged; in this direction particularly, adsorption data would be of very great assistance. Suppression of catalytic effect by complete covering of the active surface by one reactant alone could also be predicted.

The velocity of reaction.

The speed with which a heterogeneous reaction takes place depends primarily on the activity of the catalyst employed, but in cases involving more than a single type of molecule the observed velocity will be determined by the slowest stage of all those involved. An interesting example of this has been described by Emmett and Brunauer,[1] who measured the adsorption of nitrogen on iron catalysts, and found that the rate of ammonia synthesis was of the same order as that of nitrogen adsorption. The energy of activation of the adsorption process was found to be 51 kilogram-calories, a figure in very close agreement with that stated by Winter[2] as the energy of activation for the decomposition of ammonia by an iron catalyst, in which he deduced that the rate-controlling step was the desorption of nitrogen. The results were also found to be in agreement with those of Emmett and Love[3] for the decomposition of iron nitride.

Selection of promoters and carriers.

The choice of a satisfactory promoter appears to depend chiefly on the physical properties of the compound employed, such as solubility in water. The possibility of chemical reaction between the promoter and the catalyst must be considered and avoided, but the proper exploration of one or two promoters will obviate the necessity for a complete survey of

---

[1] *J A.C S.*, 1934, 56, 35

[2] *Z. phys. Chem.*, 1931, 13 B, 401.

[3] *J.A C.S*, 1933, 55, 4043.

the whole range which may be available. The question of carriers becomes important in the commercial development of a catalytic process, and for this reason their mechanical properties are of most importance in a final selection.

Development of experimental investigation.

By way of a very brief summary of the information available concerning experimental methods of investigation into catalysis, an attempt will be made to indicate the directions in which further development may be looked for. These may be classified under the following headings:

1. Adsorption of reactants on catalysts.
2. Promoter action.
3. Poisoning and retardation.
4. The location of activity.
5. Compound catalysts.
6. Investigation of surfaces and structures.
7. The nature of activation.

1. *Adsorption.* The compilation of an adsorption catalogue for a large number of substances is obviously a desirable practical development, and with this purpose in mind a closer study of the stability of the catalyst compounds in contact with a variety of gases must also be considered. A comparatively slight change of conditions may easily lead to the formation of an entirely different type of active centre in the catalyst, or to complete removal of an active substance. Although certain generalities are known in the behaviour of different compounds of the catalyst element, there must always be a specific effect associated with each of these compounds; this must be identified in every case before consistent results can be hoped for.

A second question which needs much further exploration by adsorption determinations concerns the conditions under which only one of two reactants need be activated on the catalyst surface. Information on this point has a very material bearing on the use which can be made of adsorption data, and a large number of additional facts are required before any regularities can be detected.

In the direction of determination of the heat of adsorption, figures for both reactants and reaction products have been shown to be equally important because of their influence on the value of the true energy of activation for the reaction. The measurements, however, must be carried out in the same temperature range as that in which activated adsorption occurs, and for this reason it would appear easier to obtain the values by calculation from the isobar rather than by direct determination with any type of calorimeter.

With respect to the significance of activated diffusion in catalytic effects, experimental evidence is required as to the relative velocities and energies of activation for the adsorption and diffusion stages separately. Determinations with molecules of large size should prove useful in this direction.

2. *Promoter action.* More detailed examination of an authentic case of promoter action, by determination of the true energy of activation and of the relative number of active centres, would be of great interest. The results obtained would be of particular value when compared with similar information for cases such as iron-alumina-potassium oxide catalysts used for ammonia synthesis, or zinc chromate catalysts used for methanol synthesis, as these appear to be intermediate in character between normal compound formation and simple promoter action.

The use of a dilution method of investigating the action of mixed catalysts is probably restricted to reactions which involve molecules of large size, so that its application is limited to the study of organic substances.

3. *Poisoning and retardation.* Although a large number of determinations of the effect of poisons on the adsorption of reactants has been described, none of these has dealt with the conditions at elevated temperatures. It would be of great interest to observe the activated adsorption of a gas on a catalyst which was progressively poisoned, and equally important to study the results obtained when the surface was partially covered with an inhibitor which itself could be removed by evacuation. Nothing is known, too, about the action of poisons on promoted catalysts, so that a further study of this point along the lines followed by Maxted would

undoubtedly assist in the further characterization of this class of substance. The experimental investigations which have so far been largely confined to the study of metallic surfaces could be very usefully extended to oxide or other compound catalysts.

4. *Active centres.* The many different methods which have been described for direct measurement of the surface area of catalysts are all open to the objection that they do not necessarily show the extent of surface which is actually effective in the reaction; this applies even to the case where the adsorption of a gas is determined at low temperatures. There is clear evidence that individual gases are often adsorbed on quite distinct parts of a catalyst, at temperatures which are necessary to bring about chemical reaction, and the active parts of the surface, whether they are points or areas or phase boundaries, cannot therefore be evaluated except for each particular reactant in turn.

The method which depends on the determination of the heat of activation for the reaction or for activated adsorption, and calculation by means of the modified Arrhenius' equation, is far the best for comparison of the quality and number of active centres. The changes which occurred on sintering promoted catalysts could by this means be compared with those which take place with single-component surfaces, and would provide still further evidence as to the character of the active centres.

5. *Compound catalysts.* The fact that compounds have a specific activity different from that of their components has been demonstrated by the work of Huttig on mixtures of oxides, by the occurrence of poisoning due to compound formation, and by experiments with a series of substances such as chromates, molybdates, or vanadates. It is probable that these effects are associated with changes in crystal structure, but practically nothing is known as to the nature of the linkages which persist during chemical conversion of the catalyst, such as that which takes place during reduction of a metal vanadate, for example.

There is also the possibility that in compound catalysts of this type more than one active centre is coming into action at the same time, and that adsorption of two different kinds of molecule can take place simultaneously on adjacent but separate parts of the surface which do not suffer from mutual retardation. Such conditions would explain the case where no catalytic effect is exhibited by either component of a mixed catalyst, but where both together have a pronounced activity. A close study of the adsorption of reactants and of the energy relations for a reaction on this type of catalyst would assist in the further development of compound catalysts.

6. *Surface and structure of catalysts.* The application of X-ray investigation of catalysts has certain limitations which are now fully appreciated, but there remains much useful work to be done in determining the occurrence of new compounds in mixtures, and identifying the nature of the active state in a one-component catalyst. A comparison of the lattice dimensions of active oxides, for example, which have actually taken part in catalytic reaction, would indicate whether any relation existed between the atomic spacing of the solid and the size of the reacting molecule, as postulated by Balandin. The velocity of adsorption of a gas on a series of solids with a closely related but slowly changing crystal structure would also be worth determination.

In connexion with effects more strictly confined to the surface, the use of electron diffraction and microscopic methods of examination are most promising. They would be of particular interest when applied to examples of promoter action, of poisoning, and of gases held by activated adsorption.

7. *Activation.* The application of data for the energy of activation of a reaction to a study of the nature of the catalyst has been emphasized in a number of references, both to single and mixed catalysts There is also a need for fuller information regarding the change of the activation energy during saturation of the surface, as it is not yet known to what extent steric effects may lead to a gradual increase in its value.

The detection of the slowest step in a series of changes involved in a reaction is also possible by such methods of investigation, and this is of considerable practical importance in hastening a search for a new or improved catalyst.

This summary is concerned only with the theoretical side of the subject, but the degree of success attained in explaining the phenomena of catalysis will ultimately be assessed by its application to technical processes.

It may be anticipated that the development of industrial catalysis will become less empirical in character, and will make more use of results obtained by the systematic investigation of the whole subject. At the same time, the exacting conditions of large-scale production will provide a useful check on any tendency to examine exceptional circumstances in too great detail, and a stimulus for the more rapid translation of laboratory data into manufacturing practice.

INDEX

AUTHORS

Adadurov, 4, 97.
Adkins, 24.
Allen, 154.
Almquist, 78, 94, 115, 117.
Andrade, 130.
Anochin, 178.
Applebey, 81, 160, 162.
Armstrong, 72, 84, 113.
Arnold, 103, 153.
Askey, 59.
Audibert, 111, 184.

Badische Anilin und Soda Fabrik, 70.
Balandin, 85, 89, 142–5, 148, 179, 193
Baly, 85.
Balz, 117.
Barrer, 36, 53, 182
Beebe, 22, 136, 138, 168.
Benedict, 149
Benton, 26, 31, 116, 156, 187.
Berend, 139.
Black, 94, 115, 117.
Bleakney, 49.
Bodenstein, 1, 152.
Boreskov, 97.
Born, 182.
Bosworth, 150.
Bowden, 107, 134.
Bradford, 104, 127.
Bray, 25.
Brewer, 128.
Brill, 81.
Britton, 61.
Brooks, 77.
Bruce, 46, 88, 188.
Brunauer, 38, 49, 61, 95, 110, 189.
Bull, 136
Burk, 9, 103, 143, 153.
Burns, 13.

Cady, 181.
Cassel, 78.
Chapman, 104, 156.
Constable, 102, 106–8, 157, 170–1.
Crawley, 102.
Cremer, 170, 182, 185.
Crittenden, 78, 80–1.

de Boer, 128.
Dew, 25.
Doble, 59.
Dobytschin, 129.
Dohse, 171.

Eckell, 122, 129, 162, 170.
Eisenhut, 121.
Elgin, 156.
Elkin, 134.
Emmett, 33, 38, 49–51, 61, 95, 110, 116, 189.
Engelder, 120.
Evans, 105.
Eyring, 167, 169.

Fajans, 129.
Farkas, 38, 51, 97, 158.
Fenske, 3, 5.
Finch, 104, 125–7.
Fischer, 4, 104, 188.
Foresti, 178.
Fox, 59.
Frankenburger, 25, 41, 49, 61, 63, 148.
Frazer, 121.
Frohlich, 3, 5, 12, 61, 69.
Frost, 69, 129.
Fryling, 24, 135, 157.

Garner, 22, 24, 29, 118, 136.
Gauger, 127.
Germer, 147.
Gernet, 4.
Ghering, 100
Goggs, 73, 132.
Goldwasser, 168.
Gould, 49, 161
Green, 154
Gregory, 104.
Griffin, 96
Griffith, 16, 28, 39, 44, 51, 69, 73–4, 78, 80, 86, 88, 102, 112, 131, 146, 149, 158, 176, 185–6, 188.

Hägg, 121, 124.
Hahn, 184.
Hall, 136.
Hampel, 108.
Harger, 70.
Harker, 46.
Harkness, 33, 50–1.
Hassid, 136.
Hawk, 80.
Hilditch, 72, 113.

Hill, 28, 39, 51, 80, 112, 146, 176.
Hinshelwood, 1, 8, 43, 101, 147, 152–4, 156, 162–3
Hodler, 49, 61, 63.
Hollings, 44, 46, 88, 186.
Hoover, 24, 96.
Horiuti, 49, 166.
Hoskins, 25.
Hostetter, 117.
Howard, 38, 42, 46, 51.
Hurst, 63, 71.
Husson, 98, 135.
Huttig, 109, 113, 122, 140–1, 172, 175–6, 192.

Insley, 46.

Jerofejev, 67, 82.
Jijima, 37.
Johnson, 128.

Kaupp, 121.
Keunecke, 81.
Kingman, 22, 24, 53, 70, 118, 136.
Kistiakowsky, 3, 25.
Kittel, 172, 175.
Klar, 167–8.
Knudsen, 40.
Kobozev, 67, 82, 178.
Kotowski, 139.
Kuentzel, 132
Kunsman, 102, 153, 162.

Lambert, 58
Langmuir, 1, 58, 101, 116, 148, 152, 156.
Larson, 77.
Lazier, 24, 120.
Leach, 73.
Long, 121.
Love, 189.
Low, 168.

Marek, 184.
Mark, 126.
Maxted, 17, 98, 100, 136, 140, 164, 180, 191.
McBain, 19, 21, 61.
McCubbin, 103.
McKie, 22.
Medsforth, 70.
Melville, 34, 154, 169.
Merck, 92
Messner, 41.
Meyer, 4
Middleton, 3.
Mittasch, 67, 81.
Moll, 150.
Moon, 164, 180.
Morikawa, 149.
Morozov, 32.
Moses, 85.
Motz, 126.

Natanson, 82.
Natta, 81.
Neumann, 83, 148.
Nikitin, 25
Novak-Schreiber, 172.
Nyrop, 181.

O'Connor, 134.
Ogden, 49.
Ormandy, 13.
Ott, 121.

Pace, 36.
Palmer, 157, 171.
Pease, 19, 60, 70, 96, 156, 168.
Perry, 3
Pickett, 102.
Pietsch, 9, 139.
Piggot, 114.
Plant, 73.
Polanyi, 49, 166, 169, 178, 182.
Porter, 147.
Prichard, 156.

Quarrell, 126.
Quiggle, 3, 5.

Raineau, 111, 184.
Ramsbottom, 156.
Ransley, 42.
Rhead, 55.
Richardson, 63.
Richter, 123
Rideal, 24, 34, 63, 70–2, 97, 107, 135, 156, 158, 167.
Roberti, 95.
Roberts, 23, 36, 40, 138.
Rogers, 117.
Roxburgh, 154
Rubinstein, 142.
Rudishill, 120.
Russell, 100.

Sabalitschka, 85.
Sabatier, 188.
Schenck, 81–2, 117.
Schleede, 123
Schmidt, 123, 181.
Schmitt, 106, 114.
Schultes, 176.
Schwab, 80, 108, 121, 139–40, 170, 176
Scott, 73.
Seitz, 150.

Senderens, 188.
Seuferling, 9.
Shah, 57.
Sherman, 50, 167, 169.
Sickman, 138, 179.
Sieverts, 42.
Sluchovski, 82.
Smith, 80.
Smithells, 42.
Sosman, 117.
Staeger, 80, 121.
Starkweather, 115.
Steacie, 103, 134.
Stewardson, 21.
Stewart, 96
Stimson, 127.
Storch, 170.
Storfer, 121.
Strother, 31.
Strutt, 142.
Swan, 70, 132

Tammann, 129.
Taylor, G. B., 3, 115.
Taylor, H. A., 102.
Taylor, H. S., 22, 25–7, 30–1, 36, 38, 46, 49–50, 70, 72, 80, 133, 138, 149–50, 157, 161, 179.
Terry, 70.
Thomson, 126
Topley, 153.
Trillat, 126.
Trotman, 156.
Tschakert, 175.
Tucholski, 167.
Turkevitch, 38.

Ubbelohde, 117.
Ussatschev, 93.

Varga, 119
Vaughen, 120.
Vavon, 96, 135.
Veal, 118.
Vick, 128.
Volmer, 150

Wagner, 80, 121
Ward, 3, 42, 136.
Wedekind, 92.
Weisskopf, 182.
Wesselkock, 82.
Wheeler, 55, 168.
White, 26, 59, 181, 187.
Wildner, 138, 168.
Williamson, 30.
Willstätter, 150.
Winter, 189.
Wohler, 117.
Wolfenden, 127, 157.
Woodhouse, 63.
Wyckoff, 80–1.

Yoshikawa, 135.

Zelinski, 85, 101, 179.
Zimmermann, 85.
Zur Strassen, 164–5.

INDEX

SUBJECTS

Accessible area of liquid metals, 134.
Accommodation coefficient, use in surface exploration, 40.
Acetaldehyde, decomposition of, 154.
Acetophenone, hydrogenation of, 99.
Acetylenic bond, heat of hydrogenation, 53.
Activated adsorption, calculations from, 176
— — definition, 27.
— — para-hydrogen conversion and, 33.
— — predictions from, 186.
— — reality of, 42.
— — relation to catalyst activity, 24, 37, 45
Activated diffusion, 34, 191.
Activation, energy of, 135.
— — catalytic reactions and, 162–3.
— — data for calculations, 193.
— — effect of promoters on, 162.
— — *see* Energy of activation.
Active atoms, abnormal state of, 116.
— — number in iron catalysts, 95.
Active centres, adsorption on, 176.
— — calculation of number, 171–2
— — creation of, 190.
— — definition of, 133.
— — determination of number, 192.
— — number in hydrogen adsorption, 177.
— — poisoning of, 180.
— — promoted catalysts and, 176–7, 191.
— — quality of, 172.
Active compound, identification of, 190.
Activity of catalysts, comparison of, 7.
— — relation to adsorption, 24.
Activity, change during use, 144.
— coefficient, definition of, 169.
— energy of activation and, 163.
— heat of adsorption and, 136.
— number of active centres and, 172.
Adlineation, theory of, 139.
Adsorbed gas, displacement of, 29, 41.
Adsorbed layer, mobility of, 150.
— molecule, state of, 143, 152.
Adsorption, acceleration by promoter, 79
— calorimeter, 22.
— catalyst activity and, 24.
— determination by weighing, 21.
— differential heat of, 135.
— energy of activation for, 138.
— factor in Arrhenius equation, 165.
— heat of, 22, 135
— measurement of, 19.
— poisoned catalysts and, 96.
— poisoning and, 191.
— prediction of retardation from, 189
— pressure and, 60.
— reduction of oxides and, 118.
— relation to crystal structure, 144.
— retardation and, 102.
— steric effects in, 138.
— valency forces in, 183.
— velocity, catalyst activity and, 46.
— — hydrogen isotopes and, 168.
— — importance of, 28.
— — measurement of, 21.
— — promoted catalysts and, 28.
Affinity between catalyst and reactant, 145, 148, 179.
Ageing of catalysts, 129.
Alcohol decomposition, rare earth oxides for, 185.
— — retardation in, 102.
Alcohols, comparison of, 171.
— decomposition of, 157.
— dehydration of, 96, 171.
— dehydrogenation of, 96.
— — calculations from, 170.
Aldehyde, formation from alcohol, 96.
Alkali, effect on copper catalyst, 3.
— — on permeability of silica, 37.
— — on reactions of charcoal, 59.
Alumina, effect on crystal structure of iron catalyst, 122
— — on decomposition of iron nitride, 82
— — on reduction of nickel oxide, 114.
— gel carrier, 90.
— miscibility with iron oxide, 162.
— promoter for iron catalyst, 81.

Alumina solution in magnesia, 124.
Amalgams, catalysts made from, 46.
— electron diffraction by, 126.
Ammonia, adsorption on tungsten, 49, 61.
— decomposition on iron, 189.
— — on metals, 153
— — on osmium, 103.
— — retardation in, 102
— oxidation, catalysts for, 73, 114.
— reaction with deuterium, 50.
— synthesis, catalysts for, 17, 68, 81, 148, 188.
— — energy required for, 162.
Amorphous material in catalysts, 120
Apparatus for adsorption measurement, 19
— for dynamic experiments, 9.
— for static experiments, 8.
— for use at high pressures, 13.
Apparent energy of activation, 163.
— poisons, 67.
— volume of catalyst, 10.
Area of catalyst surface, 106, 192.
— — — change on sintering, 107.
— of iron catalyst, 110.
— of liquid metals, 134.
— total and effective, 111.
Arrhenius equation, calculations from, 29, 169, 172.
— — for catalytic reactions, 163–5.
Arsenic, poisoning of platinum by, 98.
— — of vanadium catalyst by, 98.
Atomic hydrogen, reduction of copper oxide by, 34
— spacing in catalysts, 193.
Atoms, adsorption of, 50
— existence in adsorbed layer, 127.
Autocatalysis in reduction of oxides, 116.

Back reaction, use in selecting catalysts, 11.
Barium sulphate as carrier, 85.
Bauxite as carrier, 7.
— dehydration of alcohols on, 171.
Beilbey layer, properties of, 126.
Benzaldehyde, production from toluene, 184
Benzene, adsorption on catalysts, 40.
— conversion to cyclohexane, 99, 121.
— formation from phenol, 69, 78.
— hydrogenation of, 99, 121.
— reaction with deuterium, 49.
Benzoic acid, production from ethyl benzene, 17.
— — — from toluene, 184.
Bimolecular reactions, kinetics of, 154.
Brass, formation in copper-zinc catalysts, 69.

Calorimeter, adsorption, 22.
Carbides, crystal structure of, 124
Carbon, adsorption of oxygen by, 55.
— combustion of, 55.
— deposit, removal from catalyst, 105.
— gasification in steam, 58
— interaction with carbon dioxide, 58.
— — with hydrogen, 52.
Carbon dioxide, production from carbon, 58.
— — reaction with hydrogen, 156.
— — reduction of, 70.
Carbon disulphide, adsorption on titanium sulphide, 160.
— — catalysts for hydrogenation of, 105.
— — conversion to sulphur, 184–5.
— — hydrogenation of, 188
— — poisoning by, 98.
— — reaction with sulphur dioxide, 158.
— — retardation in reaction of, 102.
Carbon monoxide, adsorption on zinc catalysts, 118.
— — catalysts for oxidation of, 70, 73, 83, 92, 123, 132, 156, 162, 174.
— — combustion, *see* catalysts for oxidation, *above*.
— — oxidation, *see* catalysts for oxidation, *above*
— — poisoning by, 96.
— — reduction of, 70, 188.
Carrier, effect on colour of catalyst, 114.
— enhanced activity due to, 66.
— mechanical properties of, 190.
— preparation of, 7
— selection of, 84, 189.
Carrier action, promoted catalysts and, 91.
— — types of, 66.
Catalyst activity and adsorption, 24, 37, 45
— affinity for reactant, 145, 148, 179.
— cleaning of, 19.
— forms used, 2.

Catalyst preparation of, 2
— purification of, 6.
— reaction with gases, 52.
— regeneration of, 15, 104.
— shrinkage of, 11, 131.
— X-ray examination of, 69, 80, 120, 193.
Catalytic reactions, kinetics of, 152.
Cathode-ray oscillograph, study of surfaces with, 129.
Chain reactions, initiation from catalyst, 178.
Charcoal, adsorption on, 53, 56.
— carrier, 7, 84.
— heat of adsorption on, 61, 136.
Charging of catalyst surface, rate of, 127.
Chemical changes in catalyst, 113.
— composition, adsorption and, 118.
Chemi-sorption, distinction from activated adsorption, 40.
Chloroform as poison, 96.
Chromium oxide, adsorption on, 38, 42.
— — catalysts, colour changes in, 114.
— — — for cresol conversion, 17.
— — — for dehydrogenation, 88.
— — heat of adsorption on, 138
— — hydrogenation catalyst, 120.
Classification of hydrogenation catalysts, 187.
Clausius-Clapeyron equation, calculation from, 28.
Clays as carriers, 7.
Clean surface, adsorption on, 40.
Coal liquefaction, catalysts for, 188.
— tar, hydrogenation of, 90
Cobalt catalyst, ammonia oxidation on, 73
— — reduction of carbon dioxide on, 82.
Coke, effect of inorganic constituents on, 58.
Cold working of metals, effect of, 129.
Collision, function in catalysis, 152.
Colloidal solutions, use for adding promoters, 6.
Colour change in mixed catalysts, 123.
— — on oxidation of catalysts, 114.
— — on reduction of oxides, 114
— of films, 107.
— relation to crystal lattice, 124
Combustion of carbon, 55.
Comparison of catalysts, methods for, 9.
Compound catalysts, development of, 192.
— — dissociation of, 69.
— — stability of, 69.
— formation between catalyst and reactant, 179.
— — colour changes and, 123.
— — crystal structure and, 121.
— — mixed catalysts and, 64, 67.
— — physical properties and, 113.
— — poisoning by, 100
Condensible vapours, gauges for, 21.
Configuration of surfaces, 133.
Congo red, adsorption by catalysts, 109.
Contact, time of, 10.
Copper, adsorption on, 63.
— — of hydrogen isotopes on, 34, 168
— catalyst, colour changes in, 115.
— — dehydrogenation on, 86.
— — methanol decomposition on, 3.
— — promoted, 80.
— — reactivation of, 100.
— decomposition of alcohols on, 171
— heat of adsorption on, 138.
— hydrogenation of ethylene on, 156
— oxide, adsorption on, 25.
— — catalyst, promoted, 80.
— — reduction of, 34.
— poisoning by carbon monoxide, 96
Co-precipitation of mixed catalysts, 4.
Cotton seed oil, hydrogenation of, 72, 113
Covering of catalyst, retardation and, 189
Cresol, conversion to toluene, 16–17, 149.
Critical concentration of promoters, 73.
Crotonic acid, hydrogenation of, 164, 180
Crystal edges, adsorption at, 139.
— growth in mixed solutions, 139.
— lattice constant, mixed catalysts and, 162.
— — empty spaces in, 124.
— — expansion in mixed catalysts, 69.
— structure of catalysts, 120–1.
— — promoters and, 80.
— — relation to colour, 124.
Crystalline form of catalyst, 3, 120.
Crystallization of catalyst, 129.
— of films, 130.

Crystals, adsorptive capacity and size, 25
— reactions on, 139.
Cyclohexane, adsorption on catalysts, 39
— dehydrogenation of, 85.
— position on catalyst surface, 144

Deactivation of catalysts, 180.
Debye pattern from mixed catalysts, 176
Deformation of crystal lattice, 129.
— of reacting molecule, 157.
Degree of promoter action, variation of, 80
Dehydration catalysts, alcohols and, 96.
— — properties of, 161
Dehydrogenation catalysts, classification of, 145.
— — energy data for, 89.
— — properties of, 161.
— of hydrocarbons, 88.
— platinum catalyst for, 85.
Dekalin, dehydrogenation of, 85.
Delayed dilution in carrier action, 88.
Density of catalysts, 111.
— — calculation from X-ray data, 112.
— relation to catalyst composition, 112.
Deposits on catalyst, removal of, 104.
Desorption, activation energy of, 161.
— from catalyst, 178.
— products from unreduced catalyst, 119.
— steps involved in, 161.
— velocity of, 161.
Destructive hydrogenation, catalysts for, 188.
Deterioration of catalysts, 129.
Deuterides, zero point energy of, 167.
Deuterium, adsorption on copper, 35, 168.
— comparison with hydrogen, 35, 167.
— exchange and ortho-para conversion, 51.
— reaction with ammonia, 50.
— — with benzene, 49.
— — with ethylene, 38, 158, 166–8.
— — with hydrated catalysts, 50.
— reduction of copper oxide by, 34.
— — of oxides by, 117.
— velocity of adsorption of, 168
Development of new catalysts, 184.
Diamond, comparison with graphite as catalyst, 121
Differential heat of adsorption, 135–6.
Diffusion, activated, 34.
— hydrogen in charcoal, 54.
— reactants to catalyst, 3.
— relation to adsorption, 32.
— through metals, 42.
Dilution in carrier action, 66, 88.
— of catalysts by carriers, 90.
Displacement of adsorbed gas, 29, 41
Drying of catalysts, 3.
Dual catalysts, 92.
Dyes, adsorption by catalysts, 108.

Electrical conductivity of surfaces, 107.
— heating of catalytic filaments, 9.
Electrode potential, measurement of surface by, 107.
Electrolytic gas, catalysts for combustion of, 70
Electron diffraction, adsorbed gases and, 193.
— — catalysts and, 193.
— — surfaces and, 125.
— emission from surfaces, 128
Electrons on catalyst surface, 181.
Elements, place in periodic system, 184.
Emissivity of surfaces, effect of gases on, 128
Empty spaces in crystal lattice, 124
Energy barrier, penetration of, 182.
— exchange with catalyst, 170.
Energy of activation, adsorption and, 138.
— — — on charcoal, 54.
— — — on promoted catalysts, 47.
— — calculation of, 29.
— — catalyst activity and, 163.
— — change during saturation, 30.
— — promoters and, 162
— — sintered catalyst and, 180.
Energy relations in catalysis, 161.
— requirements for ammonia synthesis, 162.
Eosin, adsorption by catalysts, 109.
Equilibrium, measuring rapid approach to, 128.
Etching, increase of area due to, 135.
Ethane, adsorption on catalysts, 38.
Ethyl benzene, conversion to benzoic acid, 17.
— cinnamate, reduction of, 108.

Ethylene, adsorption on copper, 38.
— exchange with deuterium, 38, 158, 166–8.
— hydrogenation of, 46, 120, 156, 164, 178.
— para-hydrogen conversion and, 97.
— production from alcohol, 96.
— reaction with deuterium, 38, 158, 166–8
Evaporation of mixed solutions, 4.
Exchange reactions with hydrogen isotopes, 38, 49, 158, 166
Exothermic reactions, dispersal of heat from, 4.
— — heat evolved in, 9
Experimental methods, developments in, 190
Extra rings in electron diffraction patterns, 126.

False equilibrium in adsorption, 187.
Fat hardening, 1.
Faults in crystals, 123.
Ferric oxide, mixtures with other oxides, 122, 172
— — rate of reduction of, 115–16.
— — -zinc oxide catalysts, 174.
Ferrites, formation in mixed catalysts, 123, 176
Filaments, heating of active, 9.
Films, colour of, 107.
— distortion by substrate, 126.
— growth of crystals in, 130.
— methods of examining, 125
First order reactions, 153.
Fission of adsorbed molecule, 144.
Fluorescence in mixed catalysts, 113.
Formic acid, decomposition of, 153, 164.
Fragments of molecules, reactions of, 179.
Fuchsin, adsorption by catalysts, 109
Fumaric acid, hydrogenation of, 85.
Fused metals, changes on solidifying, 134.

Gas layer, effect on surface potential, 127.
Gold films, properties of, 130.
Grain growth in catalysts, 81.
Graphite, comparison with diamond as catalyst, 121.
Grease, effect on electron diffraction, 126.
Heat, deactivation of catalyst by, 180.
Heat of activation, *see* Energy of activation.
— adsorption, calculation of, 28
— — change during saturation, 23.
— — data on, 136.
— — energy calculations and, 163.
— — errors in measuring, 23.
— — measurement of, 22.
— — reaction products and, 191.
— — specific effects of gases, 138.
— — temperature and, 191
— — unreduced catalyst and, 118.
Heavy hydrogen, *see* Deuterium.
Heterogeneous catalyst, difference from chain inductor, 178
— reactions, comparison with homogeneous, 152, 162
Heteropoly acids containing molybdenum, 70.
Hexane, adsorption of, 39, 43–4.
— catalysts for decomposition of, 146.
— decomposition on promoted catalysts, 75
High-frequency current, effect on catalysts, 181.
— pressure, apparatus for use at, 13.
Homogeneous reactions, comparison with heterogeneous, 152, 162
Hopcalite catalyst, 132
Hydrated catalysts, reaction with deuterium, 50.
Hydrides, crystal structure of, 124
— zero point energy of, 167
Hydriodic acid, decomposition of, 154
Hydrocarbons, adsorption on catalysts, 38–9, 146
— complex with catalyst, 49.
— decomposition on promoted catalysts, 39.
— dehydrogenation of, 88
— deposition on nickel catalyst, 105
— production from carbon monoxide, 104, 188
Hydrogen, adsorption on copper, 35.
— — on manganese oxide, 30.
— — on metals, 186.
— — on nickel, 26.
— — on oxides, 38, 186.
— — on promoted catalysts, 47.
— — on tungsten, 23.
— — on zinc oxide, 24, 31.
— combustion on metal surfaces, 156.

Hydrogen, comparison with deuterium, 158, 167
— evidence for dissociation of, 135.
— evolution from metal surfaces, 107.
— heat of adsorption on charcoal, 53.
— isotopes, reactions of, 167–9
— para-ortho conversion, 9, 50–2, 97, 130, 157
— reaction with carbon, 52.
Hydrogen peroxide, decomposition of, 99, 180
Hydrogen sulphide, decomposition of, 102
— — formation from carbon disulphide, 105, 188
— — poisoning of iron by, 93.
Hydrogenation catalysts, classification of, 181, 187
— — poisoning of, 98.
— *of ethylene, 46, 120, 156, 164, 178.*
— of tar oil, 46, 90, 119

Ignition temperature, effect on catalyst, 120
Impurities, action as poisons, 93.
— effect on adsorption by carbon, 57
— — on electron diffraction, 126.
— removal from catalyst, 6
— — by oxidation, 101
Incandescent mantles, mixed oxides in, 132
Inhibitors, *see* Retardation.
Intermediate compound formation with catalyst, 148, 182.
Intrinsic catalyst activity, 170
Inversion of temperature coefficient, examples, 167.
Ionization currents of surfaces, 127.
Iron, adsorption of hydrogen on, 25, 32.
— — of nitrogen on, 38, 62
— catalyst, adsorption at low temperatures on, 110.
— — crystal structure of, 122.
— — equilibrium with steam, 115.
— — mixed promoters for, 77.
— — oxidation of, 117.
— — poisoning of, 93–4.
— — surface of, 110.
— crystals, adsorption and size, 25.
— — reaction with nitrogen, 121
— decomposition of ammonia on, 102.
Iron nitride, decomposition of, 82
— — formation in ammonia catalysts, 160.
Iron oxide, reduction by hydrogen, 117.
— — *see* Ferric oxide.
Iso-amyl alcohol, decomposition of, 142.
Isobars for activated adsorption, 27, 48
Isomers, comparative results with, 149
Isomorphism in mixed catalysts, 81.
Iso-propyl alcohol, comparison with primary alcohols, 158
Isotopes, adsorption of hydrogen, 168
— energy relations with, 167–9.
— zero point energy of, 182.

Kieselguhr as carrier, 84.
Kinetics of catalytic reactions, 152.
— study of, 7.

Lattice constant, adsorption and, 144
— — catalyst properties and, 121, 193.
— — *see* Crystal lattice.
Liquid metals, area of, 134.
Loss of catalyst activity, 129, 180.

Magnesia as carrier, 86.
Magnetic susceptibility of catalysts, 112
Maleic acid, hydrogenation of, 85
Manganese oxide, adsorption on, 25, 30.
— — catalyst for ammonia oxidation, 114.
Melting-point, change in catalyst at, 134.
Mercury, effect on mobility of films, 130
— poisoning of platinum by, 99
— surface amalgams with, 126.
Metal salts, chemical changes on reduction of, 192.
— surfaces, measurement of, 107.
Metals, adsorption of hydrogen on, 186.
Methane, adsorption on catalysts, 38
— — on charcoal, 61
— equilibrium with carbon and hydrogen, 54.
— production from carbon disulphide, 188
— reaction with deuterium, 49.
Methanol, decomposition of, 3, 5, 123.
— synthesis, catalysts for, 11, 13, 184, 188.

Microbalance, adsorption measurement with, 22.
Microscopic examination of catalysts, 126, 193.
— — of films, 125, 130.
Migration in films, 130.
— of surface atoms, 150.
Mixed catalysts, active centres in, 172–6
— — adsorption on, 25.
— — — of dyes on, 108.
— — compound formation in, 64, 122, 172.
— — effect of heating, 123.
— — physical properties of, 123.
— — preparation of, 5.
— — reduction of, 115.
— — simultaneous reactions on, 142.
— — X-ray investigation of, 193.
— crystals, formation in catalysts, 81.
— oxides, catalysts from, 172, 192.
— — reduction of, 115.
— solutions, precipitation from, 72.
Mixtures, adsorption of gases from, 62.
Mobility of adsorbed layer, 150, 181.
— of gases in metals, 36.
— of surface films, 130.
Molecular fragments, reactions of, 179.
Molecule, activation on catalyst, 178.
— attachment to surface, 143.
— orientation on surface, 147.
— size, alcohol decomposition and, 157.
— — carrier action and, 88.
Molecules held by surface, number of, 170.
Molybdenum catalysts, active centres in, 177.
— — ammonia synthesis on, 68.
— — from heteropoly acids, 70.
— — sulphur and, 119.
— oxide catalysts, adsorption on, 28.
— — — promoters for, 39.
— — — structure of, 80.
Monatomic films on tungsten, 148.
Multiple-promoted catalysts, 77.
Multiplet theory, 144.

Nickel, adsorption of dyes on, 108.
— — of hydrogen on, 26
— -alumina catalysts, 142.
— catalyst, composition of, 113.
— — ethylene hydrogenation with, 154.
Nickel catalyst, reduction of carbon dioxide with, 82.
— determination of surface of, 108.
— heat of adsorption on, 135.
— oxide, promoting action of, 83.
— — reduction of, 113, 116.
— poisoning of, 95, 104, 135.
— rate of solution in acids, 108.
Nitric oxide, adsorption on charcoal, 57.
— — decomposition on platinum, 154.
Nitrides, crystal structure of, 124.
— formation in ammonia synthesis, 148.
Nitrobenzene, reduction of, 98–9, 135.
Nitrogen, adsorption on catalysts, 189
— — on iron, 38.
— — on tungsten, 41, 49.
— reaction with volatilized metals, 148.
Nitrous oxide, decomposition on mixed oxides, 172, 175–6
— — — on platinum, 103, 153.
— — reaction with hydrogen isotopes, 169.
Non-uniformity of catalyst, evidence for, 134.
Number of active centres in catalysts, 177.

Order of reaction, change with pressure, 153.
Organic molecule, activation of links in, 149.
— — decomposition of links in, 145.
Orientation of adsorbed molecule, 147.
— of films on substrate, 126.
Ortho-hydrogen, *see* Para-hydrogen.
Osmium, decomposition of ammonia on, 103.
Oxidation catalysts, classification of, 184.
— of ammonia, catalyst for, 114.
— of carbon monoxide, catalysts for, 70, 83, 92, 123, 132, 156, 162, 174.
— of catalyst, regeneration by, 16.
— removal of surface impurities by, 101.
Oxidation-reduction, changes due to, 1, 108.
Oxide catalysts, adsorption on, 38, 186.
— — resistance to poisoning, 149.
— — *see* Mixed oxides.

Oxides, rate of reduction of, 131.
— reduction to active state, 113.
Oxygen, adsorption on carbon, 55.
— — on tungsten, 40.
— poisoning of iron by, 94.
— reaction with hydrogen isotopes, 169
Ozone, catalytic decomposition of, 142.

Palladium catalyst, hydrogenation with, 85.
— — retardation on, 104.
Para-hydrogen, conversion of, 9, 50, 52, 157.
— retardation in conversion, 51, 97.
— sintering of catalyst for, 130.
Paramagnetism, appearance in mixed catalysts, 113.
Particle growth in promoted catalysts, 131
— size in catalysts, 129.
Paste, use in preparing catalysts, 2.
Pellets, preparation of, 2.
Periodic system, catalyst elements and, 184
Permanent poisons, 93.
Phase boundaries, in mixed catalysts, 176.
— — properties of, 124, 139.
Phenol, conversion to benzene, 69, 78.
Phenols, catalysts for conversion to hydrocarbons, 188.
Phosphine, decomposition of, 154.
Photoelectric properties of surfaces, 128, 150.
Phthalic anhydride, production from xylene, 17.
Physical properties of mixed catalysts, 123
Piperonal, hydrogenation of, 98.
Platinum, adsorption of carbon monoxide on, 156.
— — of cyclohexane on, 144.
— catalyst, deactivation of, 180.
— — dehydrogenation on, 85.
— — poisoning by arsenic, 98.
— — — by mercury, 99.
— films, structure of, 125.
— heat of adsorption on, 136.
— poisoning of, 98–9.
Poison, chemical changes due to, 119.
— concentration of, 98.
— energy effects and, 180.
— removal of, 95.
— reversible, 93.
Poisoned catalysts, adsorption on, 96.
— — energy relations for, 100.
— — regeneration of, 100.
Poisoning, apparent, 67.
— coefficient, 99.
— compound formation and, 64.
— from reactants, 93.
— prediction of, 189.
— progressive, 98
— study at elevated temperatures, 191
Poison-resisting catalysts, 119.
Polymerization products, fouling of catalyst by, 17.
Porosity of catalysts, 123.
Potential of catalyst surfaces, 127.
Precipitation of catalysts, 2.
Prediction of catalyst action, 186.
Preheating of reactants, 2.
Pressure, effect on adsorption, 60.
— — on order of reaction, 153.
Primary alcohols, decomposition of, 157.
— reaction products, decomposition of, 18.
Products of reaction, adsorption of, 191
Progressive poisoning, 135.
Promoted catalysts, active centres in, 177.
— — adsorption on, 28, 47.
— — carriers and, 91.
— — density of, 112.
— — para-hydrogen and, 51.
— — preparation of, 4.
— iron catalysts, adsorption on, 33.
— — — ammonia synthesis on, 191
— — — exchange reaction on, 50.
Promoter, acceleration of adsorption by, 79.
— action and active centres, 140, 176–7, 191.
— — theory of, 80.
— — types of, 65.
— addition as colloid, 6.
— *alternative substances as*, 74.
— atoms, ratio to catalyst atoms, 76.
— concentration of, 70, 74.
— — activity and, 39.
— — adsorption and, 40.
— — significance of, 141.
— — two reactants and, 78.
— — variation with reaction, 78.
— covering of surface by excess, 80.
— crystal structure and, 69, 80, 121.
— definition of, 65, 70.

Promoter, deposition by reaction, 6.
— energy effects with, 162.
— second, 77.
— selection of, 189.
— solubility in catalyst, 141.
— specific effects of, 71.
Propyl ketone, hydrogenation of, 98.
Pumice as carrier, 84.
Pyrophoric iron, adsorption on, 25.
— properties of catalysts, 129.

Quality of active centres, 172–7.
Quantum mechanics, deductions from, 182.

Radicals, adsorption on surfaces, 144.
Rare-earth oxides as catalysts, 185.
Rate-controlling steps in catalysis, 179.
Reactants, activation of, 190.
— affinity for catalyst, 148, 179.
Reaction chains, propagation from catalyst, 178.
— kinetics, study of, 7
— product, heat of adsorption, 191.
— removal from system, 8.
— temperature, adsorption at, 26.
— velocity and activation energy, 163
— — on sintered catalysts, 107.
Reactivation of poisoned catalysts, 15, 100, 104
Recovery of adsorbed gases from charcoal, 57.
Reduction of catalyst, temperature effect, 170.
— of copper oxide, carrier and, 87
— of oxides, impurities and, 67
— — poisoning and, 101.
— — rate of, 115, 131.
Regeneration of catalysts, 15, 104.
— of poisoned catalysts, 100, 104.
Retardation, 101.
— consequences of, 46.
— correction in energy calculations, 163.
— excessive adsorption and, 48.
— prediction from adsorption, 189.
— reaction order and, 153.
— removal of product causing, 157.
Reversible poisoning, 93.

Second order reactions, 154.
Secondary reactions, effect of, 11.
Selection of carriers, 189.
— of catalysts, 11, 186.
— of promoters, 189.
Selective combustion, catalysts for, 71.
Shape of catalyst pellets, 3
Shrinkage of catalyst, 11, 131.
Silica, diffusion through, 36.
— gel promoter, 74
Silver films, properties of, 130
— manganite, poisoning of nickel oxide by, 83
— oxide, decomposition of ozone on, 142.
Simultaneous adsorption of two reactants, 62, 92, 158.
Sintering, disappearance of active centres from, 192.
— of platinum catalyst, 180.
— prevention of, 80, 87.
— progressive, 107.
— relation to melting-point, 134.
Skeleton catalysts, 4.
Slip planes, passage of gases through, 37.
Smekal cracks, 43, 142.
Sodium carbonate, reactivity of coke and, 58
— mobility on tungsten, 150
Solid solutions in mixed catalysts, 82, 117.
Solids, reactions between, 116
— — with solutions, 139.
Solution of gases in solids, 41.
Sorption balance, 21.
Space-time yield, 10.
Specific poisons, 96
Spinels, crystal structure of, 124.
— properties of, 81.
Sputtered catalysts, structure of, 125.
Static methods of experiment, 1.
Steam, reaction with carbon, 58.
Stereo-isomers, formation in catalysis, 150.
Steric effects in activation, 193
— — in adsorption, 138
Streaming methods of experiment, 2
Substrate, effect on film structure, 126.
Sugar charcoal, adsorption on, 57.
Sulphide catalysts, resistance to poisons, 149
Sulphides, use as catalysts, 119.
Sulphur, action on molybdenum catalyst, 119.
— compounds as poisons, 104.
— production from carbon disulphide, 184.
Sulphur dioxide, adsorption on titanium sulphide, 159.

Sulphur dioxide, catalysts for oxidation of, 97, 148
— — reaction with carbon disulphide, 158, 185.
— — retardation in reaction of, 102.
Supported catalysts, *see* Carrier.
Surface change in mixed catalysts, 39.
— combustion, 132
— complexes in carbon combustion, 56
— covering by reaction products, 101.
— film, mobility of, 130
— ionization currents of, 127.
— layers, 125
— measurement by electrode potential, 107
— potential, effect of gases on, 127
— potential of deposited catalyst, 86

Tar oil hydrogenation, 46, 90, 119.
Temperature coefficient, inversion of, 167
— effect on adsorption, 26
— — on catalysts, 16, 18.
— — on orientation of molecules, 147.
— — on precipitation, 3
— — on reduction of oxides, 170.
Thermal conductivity of gases, 9.
Thiophene, poisoning by, 95.
Thoria catalyst for combustion, 132.
Three-phase systems, 1.
Three-stage adsorption, 31
Time-activity curves for catalysts, 15.
Time, change of catalysts with, 131.
Tin vanadate as oxidation catalyst, 17.
Titanium oxide catalyst, carrier action with, 87
— — decomposition of hydrocarbons on, 45
Toluene, production from cresol, 16–17, 149
True energy of activation, 163.
Tungsten, adsorption on, 23, 40–1, 61
— -bronze, structure of, 124
— complex with ammonia, 49
— mobility of sodium on, 150
Tunnel theory, 182
Two-component catalysts, preparation of, 5
— — *see* Mixed catalysts.
Two reactants, activation of, 190.
— — adsorption of, 92, 158.
— — kinetics of reaction, 155.
— — prediction of catalysts for, 188
— — promoted catalysts for, 78
— — simultaneous adsorption of, 45.

Unadsorbed molecule, collision with surfaces, 155.
Unimolecular layer, changes in, 128.
— — measurement of, 110.
— reactions, 153.
Unreduced catalyst, adsorption on, 118
Uranium nitride, poisoning of, 94.

Valency bonds at surface, 134
— forces in adsorption, 157, 183.
Vanadium catalysts, oxidation reactions on, 17.
— — poisoning of, 97
— — phenol hydrogenation on, 17, 149
— — sulphur trioxide formation on, 148
— oxide, regeneration of, 16
Van der Waals adsorption, effect of activated adsorption on, 33.
— — — on activated adsorption, 42.
— — reaction and, 181.
— — reversal of, 29
Vapour phase oxidation, catalysts for, 184
Velocity constants, adsorption on charcoal, 55.
— of adsorption, calculations from, 29
— — importance of, 179.
— — measurement of, 21.
— of reaction and activation energy, 163
— — appearance of maximum, 164.
— — factors affecting, 189.
Volume of catalyst, apparent, 10.

Water in catalysts, reaction with deuterium, 50.
— poisoning of iron by, 93
Water-gas reaction, adsorbed water and, 170
— — kinetics of, 156
Wire catalysts, control of temperature of, 9
— — preparation of, 1.

X-rays, effect of promoters on, 80.
— examination of catalysts by, 69, 80, 120, 193.
— *see* Crystal structure.
Xylene, conversion to phthalic anhydride, 17.

Zero order, reactions of, 153.
Zero-point energy, catalytic reactions and, 167–9.
— — diffusion and, 36.
— — of isotopes, 182.
Zinc, activity at melting-point, 134.
Zinc catalyst, reduction of, 118.
— oxide, adsorption of hydrogen on, 138.
— — -chromium oxide adsorption on, 24, 29.
— — methanol catalyst, 13, 191.
— — -copper, methanol catalyst, 12
— — heat of adsorption on, 138.
— — methanol catalyst, 69, 123.
— — -molybdenum oxide, adsorption on, 37.
— — reduction to metal, 117.

PRINTED IN GREAT BRITAIN AT THE UNIVERSITY PRESS, OXFORD
BY JOHN JOHNSON, PRINTER TO THE UNIVERSITY