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STUDIES ON THE SYNTHESIS AND REACTIONS OF SOME
SIMPLE AND COMPLEX HYDRIDES OF THE ALKALI METALS

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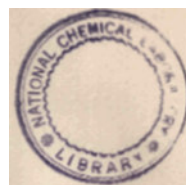
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CHAPTER 1 - GENERAL INTRODUCTION

GENERAL INTRODUCTION

Family of hydrides

Though our knowledge of hydrides dates back to the time of Davy and Gay-Lussac, the monumental work of Stock¹ on "boron hydrides" and the more recent outstanding researches on complex hydrides² by Schlesinger and co-workers in America and Wiberg and co-workers in Germany brought into prominence these much-sought-after compounds of the present day. Following World War II, intensive programmes on research and development of chemical fuels for guided missiles were launched both in the United States and the Soviet Union. For the speed and range requirements of these vehicles, the conventional fuels proved to be entirely inadequate in their energy content. On account of their high heats of combustion attention was focussed on the boron hydrides and their derivatives. As a result, multi-million-dollar plants for the production of such types of compounds were installed in the U.S. within the last eight years.

The very selective nature of reductions of organic compounds by metal hydrides, particularly the complex metal hydrides discovered in recent years, has made these hydrides indispensable chemicals to the modern synthetic chemist. To-day the organic chemist

has before him a wide spectrum of reducing agents (complex hydrides) from which he can select one to achieve a specific reduction.

The term 'hydride' is currently used for those compounds which involve a metal or metalloid-hydrogen bond, to exclude from its purview the hydrogen compounds of non-metals e.g., ammonia, phosphine, water, hydrogen halides, hydrogen sulphide, hydrogen selenide etc. The properties of compounds of hydrogen differ markedly with the nature of the combining element and as such the very differences among the various hydrides have led to several attempts for their classification³⁻⁶. The hydrides are broadly divided into three principal categories: (i) ionic or saline hydrides, (ii) covalent hydrides - the covalent molecular and the covalent polymeric, and (iii) the metallic hydrides. Table I shows the correlation between the groups of hydrides and the Periodic Table^{7,8}.

Although no sharp line can be drawn between each of the groups of hydrides the first two, namely, the ionic and the covalent hydrides, stand out as almost homogeneous groups on the basis of nature of bonding in them and attendant physical properties. The metallic hydrides are considered as a group largely out of convenience, since there are wide variations in the nature and properties of these compounds. Mention may be made about a fourth class of hydrides, the hydrides of

Group IB and IIB elements, called the "borderline hydrides" by Hurd⁵.

Superimposed on the above classification, the hydrides may be grouped in two classes to distinguish the simple or primary (binary) hydrides from the complex derivatives of some of them, called the complex or secondary hydrides, for instance, sodium borohydride NaBH_4 , Lithium aluminohydride, LiAlH_4 etc. Table II shows the overall classification of hydrides at a glance.

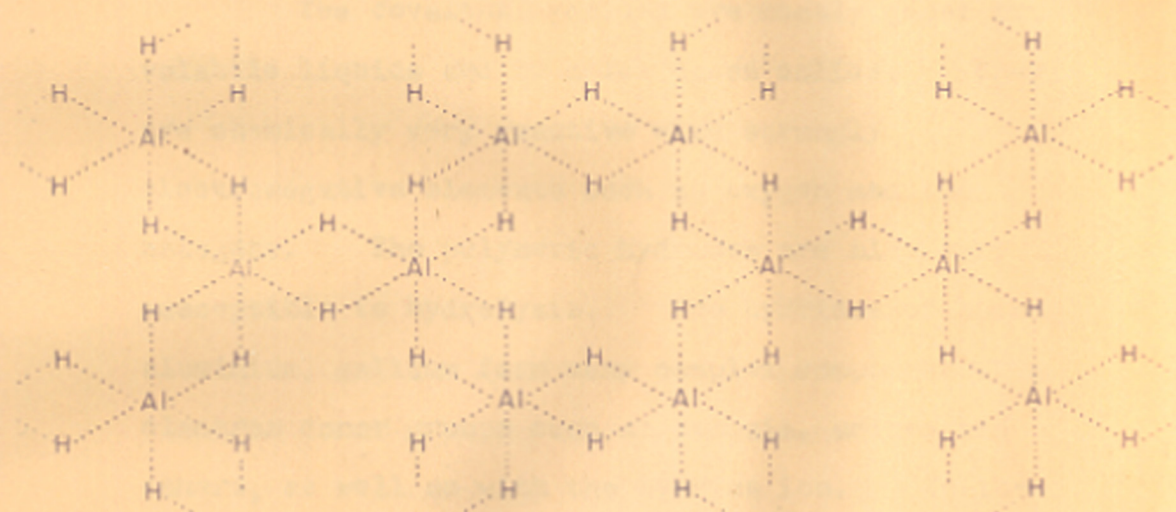
Primary hydrides

The ionic hydrides, as the name suggests, have predominantly ionic bonding and consequently possess the characteristics of ionic compounds in general. The hydrides of alkali and alkaline earth metals which belong to this group have high melting points, high heats of formation, high thermal stability, conduct electricity when melted, resembling very much in physical properties to the corresponding halides. All the alkali metal hydrides have face-centered cubic lattice structure analogous to that of sodium chloride. This similarity between the ionic hydrides and halides is best explained by considering molecular hydrogen as the weakest acid of the series HI , HBr , HCl , HF , H_2 and the hydrides as salts of this very weak acid with a strong base. Being salts of a weak acid they are susceptible to hydrolysis and, in fact, react vigorously, some explosively, with water. Except lithium hydride which exhibits covalency

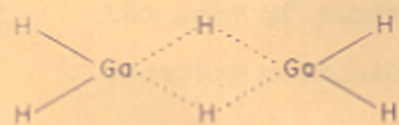
to certain extent and is soluble in polar organic solvents such as diethyl ether, they are insoluble in organic solvents.

The ionic hydrides have found several industrial applications. Lithium, sodium and calcium hydrides are used as reducing or condensing agents in the organic fine chemical industry and as polymerisation catalysts. Sodium hydride and calcium hydride find use as reducing agents in metallurgy. Lithium hydride and calcium hydride are valuable as hydrogen sources for the inflation of balloons. Ionic hydrides, particularly lithium hydride, besides finding use as constituent of rocket fuels, have also attracted considerable attention as neutron moderators.

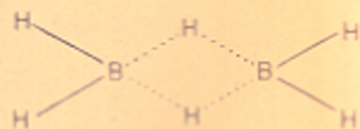
The covalent hydrides derive their name from the nature of chemical bonding in them which is primarily of the non-polar electron-pair sharing type. The hydrides of elements of Groups IIIB, IVB and VB belong to this category. The hydrides of Gr.III elements, that is, boron, aluminium and gallium (indium and thallium do not form stable hydrides) distinguish from the rest of this class of compounds by the fact that no mononuclear hydrides are observed; the simplest hydrides are dimers - diborane, B_2H_6 and digallane, Ga_2H_6 , although compounds of the type $BH_3.CO$ (borane carbonyl) and $BH_3.N(CH_3)_3$ are known. Aluminium hydride forms highly polymeric systems and low-polymeric weight forms are observed only as etherate compounds. The polymeric nature of these electron-



ALUMINIUM HYDRIDE



DIGALLANE

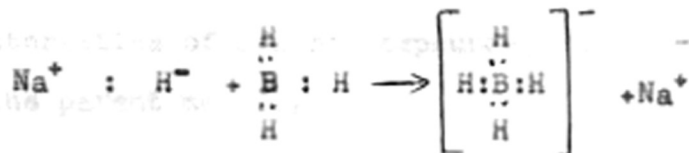


DIBORANE

FIG. 1.

deficient compounds has been explained by the hydrogen-bridge bonding theory⁹ on the basis of which the structures for diborane, digallane and aluminium hydride may be represented as shown in fig. 1. The covalent hydrides of IVB and VB group elements, SiH_4 , GeH_4 , SnH_4 , SbH_3 , BiH_3 etc. are simple monomeric compounds.

The covalent hydrides are mostly gases or volatile liquids and in a few cases solids. They are chemically very reactive with strongly electronegative elements such as oxygen and the halogens. The polymeric hydrides are also very susceptible to hydrolysis. The hydrides of boron, aluminium, gallium form many complex compounds with electron donor groups such as ammonia, amines and ethers, as well as with the hydride ion. In the borohydride, BH_4^- and the aluminium hydride ion, AlH_4^- , the alkali metal hydrides serve as the source of hydride ion which coordinates or donates a share in its pair of electrons to the central atom of the acceptor molecule.

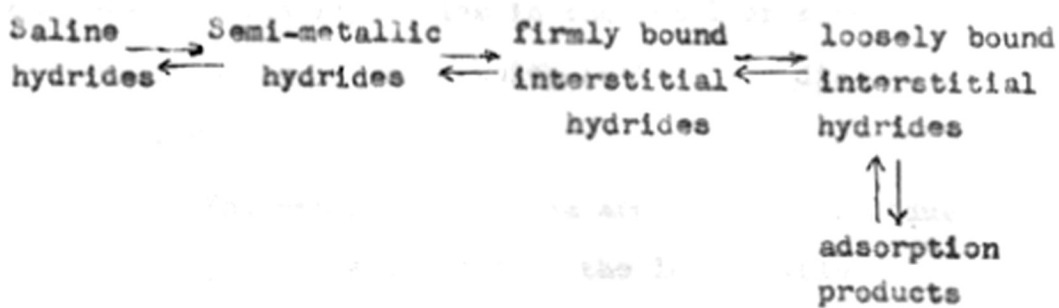


Physical studies such as infrared and Raman spectra^{10,11} and X-ray diffraction¹² have indicated a tetrahedral structure for these complex hydride anions.

Mention has already been made about the utility of boron hydrides as high-energy or exotic fuels. In addition they find important use in boron coatings useful in a variety of applications where hard, abrasion-, or corrosion-resistant surfaces are desired. The hydrides of silicon, germanium etc. have recently found application in the preparation of high purity metals required in electronic devices.

Direct Metallic hydrides are characterized by their metallic character in that they possess hardness, lustre and electrical conductivity. Although the lack of stoichiometry that is generally observed in them led them at first to be considered as interstitial materials, structural studies have shown them to be, except in a few cases, definite chemical compounds. Sieverts' studies¹³ have shown some of these compounds to be salt-like, with high heats of formation and other characteristics of saline compounds, but less dense than the parent metals.

The variations in individual properties among the metallic hydrides suggest more or less continuous transitions in the manner in which hydrogen is held according to the scheme



with all the products except the saline hydrides being called alloy-like or metallic. The semimetallic hydrides represent transitions between true chemical bonding and interstitial alloys and embrace hydrides derived from the metals in Periodic groups IVA & VA. Hydrides of the lanthanide and actinide elements provide a direct transition between these materials and the true saline hydrides. In such materials, hydrogen may well be present both as such and also bonded to the metal ions. Among the interstitial hydrides, the firmness with which hydrogen is held varies. It appears to reach maximum values with nickel, palladium and platinum.

Studies on Uranium hydride, UH_3 , led Rundle¹⁴ to extend the hydrogen bridge theory proposed earlier for compounds like boron and aluminium hydrides, also to some of this class of compounds. However, in the light of more recent neutron diffraction studies¹⁵, the same author has discounted his original conception. Preparation of stoichiometric hydride of titanium, TiH_2 , led Gibb¹⁶ to attribute the non-stoichiometry in some of these ^{compounds}, if not all,

compounds to the impurities in the metal or more seriously in the hydrogen which inhibit the dissolution of hydrogen.

The metallic hydrides are all strong reducing agents. Hydrogen evolved from the less stable metallic hydrides has great reducing power and is thought to be in atomic state in the case of palladium hydride, etc. Titanium and zirconium hydrides are used in the manufacture of vacuum tubes. The finely divided material in a suitable vehicle is sprayed onto parts of the tube which is then flashed under vacuum, thus leaving a film of metal which acts as a "getter" during subsequent operation of the tube. Titanium hydride is also used in powder metallurgy where it is said to decrease the porosity of sintered compacts. The principal advantage of the hydrides of titanium and zirconium over the powdered metals themselves is the lessened hazard of handling as the powdered metals are quite pyrophoric. Both titanium and zirconium hydrides are hydrogenation catalysts. The high hydrogen density at high temperatures of the hydrides of zirconium and cerium (and of several less common metals) suggests their possible applications for the slowing down of neutrons in shields or moderators.

Complex hydrides

The 1940's saw discoveries of a number of new hydride compounds, especially complex metal hydrides, starting from the borohydrides of aluminium and beryllium. Of these the alkali metal complex hydrides were so interesting that the vigorous research that followed their discoveries have made them indispensable tools to chemists and technologists of to-day. The first complex hydride of the alkali metal to be prepared was lithium borohydride. The relative scarcity of the lithium metal turned the attention to its next of kin, sodium, the borohydride of which was synthesized soon after. Potassium borohydride followed suit. The synthesis of lithium aluminium hydride immediately after, to be followed by that of sodium aluminium hydride, was another landmark in the history of hydrides. The extensive literature available to-day on the applications of these alkali metal complex hydrides and the increasing number of patents taken covering many of these applications to industrial problems attest the growing importance of these materials to research and industry.

The greatest interest in the complex metal hydrides has been in the reduction of organic compounds and honour of being first in this respect goes to lithium aluminium hydride. Lithium aluminium hydride is an extremely powerful reducing agent and successful organic

reductions have been carried out when other methods have had indifferent or no success. Reductions can generally be carried out at room temperature or in refluxing ether or tetrahydrofuran without the use of unusual equipment and no side reactions such as polymerization, condensation, and cleavage, often encountered with other reducing agents, occur except in isolated instances. The reactions are rapid and almost quantitative in most cases and yield very pure products owing to the absence of side reactions. The types of functional groups which are reduced under normal conditions¹⁷ are summarized in Table III. Carbon to carbon double bonds are generally not attacked by the hydride, and this permits selective reductions of functional groups in unsaturated compounds. By combining other reagents with it, mixed hydride systems are achieved that can be used to increase selectivity.

Lithium aluminium hydride has been found to provide a convenient and efficient method for the preparation of hydrides of silicon, germanium, tin etc. The major commercial uses for this substance have been in the pharmaceutical industry for the reduction of Vitamin A ester to the alcohol, for the preparation of intermediates to other vitamins, and to carry out reductions in the preparation of cortical hormones. A minor use is for the preparation of fine chemicals. Olefins add directly to lithium aluminium hydride to form the tetraalkyl derivatives. These have been used in catalyst systems for the synthesis of polyolefins and diolefins.

Sodium aluminium hydride has been found to possess properties similar to the analogous lithium compound¹⁸, except that it is somewhat more stable toward thermal decomposition; lithium compound decomposes at temperature above 125°C to aluminium, hydrogen and metal hydride whereas the sodium compound is stable up to 140°C. Due to its insolubility in ether, the reductions are generally carried out in tetrahydrofuran. Sodium aluminium hydride has not yet found appreciable applications in research and industry compared to the lithium compound, and has not been produced commercially although a new direct synthetic method¹⁹ has been reported recently.

Of the borohydrides, the sodium compound has the greatest practical interest. Chaikin and Brown²⁰ were the first to report the use of this compound in the reduction of organic compounds, namely, aldehydes, ketones and acid chlorides. The work was soon extended to other functional groups. As seen from Table IV a considerably smaller number of functional groups are reduced with sodium borohydride than with lithium aluminium hydride¹⁷. This lower reactivity has been advantageous in permitting selective reduction of groups such as the carbonyl or acid chlorides groups in the presence of functional groups which would be reduced with the aluminohydride but which are not attacked by the borohydride.

Brown and Subba Rao²¹ have reported that the addition of certain metal halides to a solution of sodium borohydride in tetrahydrofuran or the dimethyl ethers of diethylene or triethylene glycol results in a facile reduction of organic functional groups not normally reduced by the borohydride alone.

Another advantage that sodium borohydride has offered is that aqueous systems can be utilized for the reductions since the compound, unlike the aluminohydrides, is very soluble in cold alkaline water with little decomposition. Reductions are usually carried

out in water, methanol, dioxane, tetrahydrofuran and dimethyl ethers of diethylene and triethylene glycols. The borohydride is not appreciably soluble in diethyl ether, dioxan, ethyl acetate etc. It is very soluble in liquid ammonia and in the lower aliphatic amines.

A number of metathetical reactions involving sodium borohydride take place in water or in an organic solvent. These metathetical reactions are summarized in Table V.

Considerable commercial applications have been found for sodium borohydride. Its major use, involving its reducing capacity of organic compounds, has been in the pharmaceutical industry - for the preparation of vitamins (A & B₁₂), the cortical hormones, antibiotics and fine chemicals. Its ability to reduce dyes has been made use of in the dyeing of hair and wool. It is also used in hair waving preparations. Sodium borohydride is being used effectively as a reducing bleaching agent for wood pulp, cellulosic textile materials and for stabilising bleached materials to prevent colour reversion or yellowing.

The borohydride reduces nickel and cobalt salts to metals or their borides. This has been made use of in (i) chemical plating of these metals upon both metals and non-metals such as glass, ceramics and plastics, and (ii) boriding metal surfaces. The borides of nickel and cobalt etc. have been found as good

hydrogenation catalysts. Although hydrolysis of sodium borohydride is very slow at ordinary temperatures, rapid hydrolysis occurs at higher temperatures to liberate 2.37 liters of hydrogen (at S.T.P.) per gram.

Acidic compounds such as boric oxide, oxalic acid, aluminium chloride, phosphorus pentoxide etc. and metal salts such as cobaltous, nickelous, ferrous and cuprous chlorides have been found to be effective catalytic accelerators for hydrolysis. Pellets containing borohydride and these compounds are used as convenient sources of hydrogen where use of compressed gas is not possible. This hydrolysis reaction has also found use in the foaming of rubber, plastics and inorganic materials such as sodium silicate.

Although potassium borohydride seems to have almost identical properties as NaBH_4 , its use is restricted only to aqueous solutions since its solubility in organic solvents is very much less. It stands next to sodium compound in importance. Lithium borohydride has not acquired as much importance as the sodium or potassium compounds. It is a more powerful reducing agent than sodium borohydride, but is milder than lithium aluminium hydride. The reagent, unlike the sodium and potassium compounds, is soluble in diethyl ether and tetrahydrofuran.

Handling of hydrides

Handling of the hydrides, particularly those of the alkali metals, poses a problem on account of the high reactivity of these compounds towards moisture and oxygen. The large volume of hydrogen that these compounds give out on reaction with water, along with the high heat of reaction, make them potentially dangerous. However, with the various techniques and devices developed, and the necessary precautions taken, hazards involved in the handling of these compounds can be eliminated.

Among those which necessitate utmost precautions from the safety point of view are the alkali metal hydrides (except the lithium compound) and the alkali metal alumino-hydrides. The problem is increased by the presence of flammable solvents generally used with these compounds. Precautions that need to be taken, therefore, are: (i) all the apparatus and containers should be thoroughly dry and purged off atmospheric air and moisture; (ii) the solvents used should be pure and dry; (iii) all the reactions with these compounds should be carried out under dry inert atmosphere; (iv) crushing, weighing, transferring etc. should be done in dry inert atmosphere in a dry box; (v) the substances should be stored in a dry place, out of contact with air and moisture; (vi) spillages of these substances must be promptly attended to by covering them with dry sand.

Care must be also exercised in disposing of the left-over residues of these substances. Containers from which these hazardous hydrides have been removed should be carried to a safe disposal area. The residues should be cautiously decomposed with proper solvents. For the decomposition of sodium hydride residues, alcohol-hydrocarbon mixtures are preferred. For lithium aluminium hydride, ethyl acetate is recommended, but wet ether or ethanol-methanol mixtures can also be used.

Protective clothing in the form of flame-proof, spark-proof coveralls, goggles (sometimes face-shields) and cloth gauntlets are recommended for use by the personnel handling these substances, since dusts are very irritating to the skin. Spillage of solutions and slurries give alkali burns if sufficiently concentrated.

Although the borohydrides of alkali metals are not dangerously reactive toward water, they must be protected from moisture during storage, preparation of solutions and reactions, to prevent loss of purity of material. Certain acid compounds, such as aluminium and boron halides, should not be brought in contact with dry borohydrides since volatile, toxic and inflammable borohydrides such as aluminium borohydride or boron hydrides may be formed.

CHAPTER 2 - STUDIES ON SIMPLE HYDRIDES

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STUDIES ON SIMPLE HYDRIDES.

Studies on the synthesis of sodium hydride and lithium hydride.

Although sodium hydride is known since the beginning of the nineteenth century, its preparation in the laboratory poses a problem even to-day on account of its high reactivity and spontaneous ignition in moist air.

Attempts of early workers, recently checked by the Russian workers²², show that the reaction between sodium and hydrogen under static conditions do not go to completion; the coating of the hydride initially formed prevents further reaction. This led to the use of sodium in a different form, in the form of dispersion of the metal over a solid or liquid diluent.

Solid diluents used^{23,24} were substances like sodium chloride, sodium carbonate, iron powder and wood charcoal. Muckenfuss²⁵ reported successful hydrogenation of sodium dispersion in inert liquids like tetralin and nujol. The method involved hydrogenation at 250°C and 500 p.s.i. pressure for several hours. Hansley and co-workers^{26,27} claimed further improvement by making use of surface active additives in the dispersions. Hydrogenation of such dispersions of sodium could be taken to completion at 280-300°C

without any superatmospheric pressure. Several synthetic methods on sodium hydride have since then been reported, particularly with reference to some catalysts. The Russian workers²² studied some mineral oils and their aromatic fractions as catalysts in the hydrogenation of sodium. Landa and co-workers²⁸ have reported molybdenum sulphide and tungsten sulphide as suitable catalysts in this synthesis. Use of phenol²⁹ and of other alkali metals (e.g. potassium³⁰) as catalysts has also been reported.

Our initial attempts to prepare sodium hydride, using indigenous white oil (from B.O.C.) were not very encouraging. The method consisted of (i) preparation of sodium dispersion in white mineral oil (B.P. > 300°C and containing a surface-active agent in small amounts) using a Morton creased flask and a high-speed stirrer, and (ii) hydrogenation of this dispersion in the same unit at temperature 280-300°C without any superatmospheric pressure. Our experiments, following the above method, yielded products dark in colour. Hydrogenation under pressure at the same temperature as also the purification of white oil used led to no improvement. On the assumption that darkening of the product was essentially due to cracking of oil at this temperature, it was thought worthwhile to study the hydrogenation at lower temperatures. Our investigation has shown that sodium metal finely dispersed in B.O.C.'s white oil or kerosene, with oleic acid as the surface-active agent,

could be converted almost quantitatively to its hydride at 150-160°C under hydrogen pressure of 400-500 p.s.i. yielding a perfectly white product. Results of some of the experiments (on 50 g. scale) are given in Table VI.

It can be seen from these results that the low-priced kerosene has the advantage of shorter reaction time over the white oil. Also the hydride could be freed more easily of the entrant kerosene by washing with petroleum ether. Sodium hydride in kerosene was useful for obtaining dry sodium hydride required for sodium aluminium hydride preparation whereas sodium hydride in white oil was useful for the preparation of sodium borohydride.

Zintl and Harder³¹ prepared lithium hydride by hydrogenation of lithium metal charged in a boat made of electrolytic iron at 600-700°C. Albert and Mahe³² prepared lithium hydride in quantities of 1 kg., by the hydrogenation of metal at 600-700°C in a specially designed reactor. The Russian workers³³ introduced further modifications to their reaction unit. Preparation of lithium hydride involving reduction of lithium compounds such as halides³⁴, hydroxide³⁵, oxide³⁶ and carbide³⁷ with hydrogen in presence of elements like Mg, Ca, Ba etc. have also been reported.

Preparation of lithium hydride was attempted under conditions similar to those employed for the preparation of sodium hydride. A fine dispersion of lithium in white oil was effected in a specially designed stainless steel reactor fitted with a high speed stirrer. Lithium stearate was used as the surface active agent and argon gas for inert blanket. Lithium dispersion was hydrogenated in Parr's autoclave at 320°C under H_2 pressure of 1000 p.s.i. at that temperature. Although 70% conversion of the metal to its hydride was observed after a hydrogenation period of twelve hours, only a 3% further increase was observed after hydrogenation for six hours more. A higher temperature which is presumably required for complete conversion could not be attained with the autoclave at our disposal. However, these experiments reveal that lithium hydride can be manufactured by a process almost parallel to that for sodium hydride.

CHAPTER 3 - STUDIES ON COMPLEX HYDRIDES

STUDIES ON COMPLEX HYDRIDES

I. Studies on the synthesis of sodium borohydride and potassium borohydride.

Though a number of methods, mostly in the form of patents, have been reported on the synthesis of sodium and potassium borohydrides, the most noteworthy contributions on the subject in recent years have been made by Schlesinger, Brown and others at the Chicago University during the second world war.

The Chicago workers were successful in synthesizing lithium borohydride by reacting diborane with lithium hydride, but their attempt to bring out a similar reaction (of diborane) with sodium hydride was a failure³⁸. However, the addition product of sodium hydride with methyl borate, the so-called trimethoxyborohydride³⁹, was found to give the desired results³⁸. The tetra-alkoxy borohydride as well as the methoxide of sodium were also found to behave similarly.



Of these three reactions, the first one is found to proceed rapidly and quantitatively and has the advantage of requiring the least amount of diborane for synthesis of the borohydride.

Further studies showed that trimethoxy-borohydride disproportionates at temperature about 230° essentially according to equation.



The reaction was, however, found to be complicated⁴⁰.

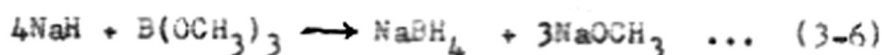
Disproportionation of trimethoxy-borohydride at lower temperature in solvents like tetrahydrofuran and diglyme (dimethyl ether of diethylene glycol), yielding sodium borohydride as one of the products, has also been reported⁴¹.



In tetrahydrofuran sodium borohydride gets precipitated, the tetramethoxy-borohydride remaining in solution. In diglyme the borohydride remains in solution while the methoxy compound gets precipitated.

Improved yields of sodium borohydride, on the basis of above disproportionation in solvents have been reported by later workers⁴²⁻⁴⁴. However, these reactions although of interest have not been utilized on a large preparative scale on economic grounds.

The highlight of the work by the Chicago scientists on alkali metal borohydrides was the synthesis of sodium borohydride by a smooth reaction⁴⁰ between sodium hydride and methyl borate, mixed in the correct proportion, at 225-275°C according to the equation,



Sodium borohydride of high purity and in good yield was extracted from the reaction mixture with anhydrous isopropylamine.

Reaction between metallic sodium, methyl borate (in proportion according to the equation given below) and hydrogen was also found to give the desired result at temperatures over 250°C and under pressure, although the yield was low⁴⁰.



Reaction between sodium hydride and boric oxide yielding sodium borohydride also formed part of Chicago work.



Yields of approx. 60% were obtained by grinding the reactants together in a small glass ball mill at 330-350°C for 20 to 48 hours. The loss of boron in the form of a product other than the borohydride, the low yields and the higher temperature of reaction are

disadvantages of the method.

Early attempts, as already stated, had failed to bring about reaction between sodium hydride and diborane. On the observation that sodium borohydride was soluble in diglyme⁴⁵, Brown examined the reaction and found that diborane readily reacted with sodium hydride in diglyme to form sodium borohydride⁴⁶.



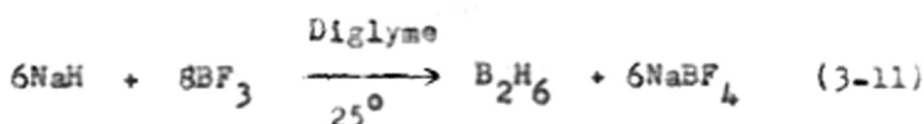
A method on the basis of above equation has been recently covered by a British patent⁴⁷.

Wittig and Hornberger⁴⁸ reported reaction between sodium hydride and boron trifluoride to yield sodium borohydride.

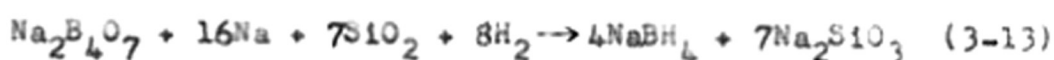


0.33 mole of sodium hydride and 0.05 mole of boron trifluoride etherate in ether were reacted in a bomb tube at 125°. Sodium borohydride in 85-90% yield was obtained. Several patents have since been taken on sodium borohydride preparation involving reaction between sodium hydride and boron halides with or without catalysts.

Brown and co-workers have reported a reaction between sodium hydride and boron trifluoride in diglyme to yield diborane⁴⁶.



Recently reports have come on German patents employing sodium borates as one of the starting materials in the manufacture of sodium borohydride. The patents cover such reactions^{49,50} as



The reactions are usually carried out at 400-500°C under pressure. Borohydride from the reaction product is extracted with solvents like liquid ammonia.

Bronaugh has patented a process⁵¹ based on the reaction between boron phosphate and sodium hydride.

A recent American patent describes a reaction of magnesium boride and alkali hydroxide to yield the alkali metal borohydride⁵².

Reactions between trialkyl borazanes, NR_3BH_3 , and alkali metal hydride, and between alkali tetraalkoxy

borate and silane to yield the corresponding alkali metal borohydride have also been reported^{53,54}.

The only reaction to find commercial exploitation for the manufacture of sodium borohydride so far is that between sodium hydride and methyl borate discovered by the Chicago workers. The Metal Hydrides Inc., Beverley, Massachusetts (U.S.A.) produces sodium borohydride on a large scale by a process based on the above reaction. However, much of the technical know-how of the process, especially the design of reactors, is trade secret. Liquid ammonia is generally used for the extraction of sodium borohydride from the reaction product on a commercial scale.

Although potassium borohydride was first prepared by Schlesinger and others³⁸ by the action of diborane on potassium tetramethoxyborohydride



its synthesis by metathesis of sodium borohydride with potassium hydroxide, covered by several patents now, appears to be more convenient and economical.



In this laboratory, the synthesis of sodium borohydride was attempted with the sodium hydride prepared by the method described earlier, by reacting sodium hydride with methyl borate essentially following

the conditions reported by Schlesinger and others⁴⁰. However, unlike these workers who used the hydride in the form of dry powder, sodium hydride dispersion in oil as such was used. The reaction product in oil, obtained at the end of the experiment, was freed of oil by several washings with dry petroleum ether (B.P. 40-60°C) and dried under vacuum. In a typical experiment 150 g. of sodium hydride was reacted and the final dry reaction product of this experiment contained 11% sodium borohydride, the total yield of the borohydride working out to be 83% on the basis of sodium hydride taken. Extraction of the borohydride was carried out with dry isopropylamine and the extracted product, obtained in 80% yield, had a purity of 75%.

Extractive ability of the solvents isopropylamine, diglyme and methylamine for the sodium borohydride in the reaction product was studied for comparison. Results are given in Table VII.

Synthesis of potassium borohydride was also attempted by direct metathesis of sodium borohydride contained in the product of reaction of sodium hydride and methyl borate. In a typical experiment in which 140 g. sodium hydride was reacted, the reaction product mixture in oil was stirred with distilled rectified spirit. Two liquid layers, one of the white oil and

the other of the alcoholic solution of the reaction product, were formed and separated. The alcoholic solution was treated with a saturated aqueous solution of potassium hydroxide to precipitate the borohydride of potassium. The product, on drying under vacuum, contained 95% KBH_4 . Yield calculated on the basis of sodium hydride was 40%. A further quantity of potassium borohydride was obtainable, in a yield of 25% more but of less purity, by precipitation from the liquor.

Reaction between sodium hydride and isoamyl borate

In view of the fact that synthetic methyl alcohol is an imported chemical and the preparation of its borate ester comparatively difficult, a reaction between sodium hydride and isoamyl borate (prepared by condensing boric acid with isoamyl alcohol, the latter obtained by fractionation of cheap fusel oil from the distilleries) was also studied.

Experiments were carried out under conditions identical to those utilized for sodium hydride-methyl borate reaction. The reaction may be written as



In a typical experiment in which 50 g. sodium hydride was reacted, the final dry reaction product mixture contained 7.5% sodium borohydride. Calculated on the basis of sodium hydride used the yield of the

borohydride worked out to be 73%.

Attempts made to isolate the borohydride from the reaction product mixture, by extracting with the usual solvents, were not encouraging. Results of experiments on extraction are given in Table VIII.

Failure to extract sodium borohydride in a pure form from the sodium hydride-isoamyl borate reaction product led us to attempt, by the metathesis of the same, to prepare the potassium salt. In a typical experiment, the dried reaction product mixture was stirred with ice-cooled absolute ethanol. The alcoholic solution was treated with excess of 10% solution of potassium hydroxide in absolute ethanol. The precipitate, after washing and drying, gave an assay 98.9% potassium borohydride. Yield was about 50% on the basis of sodium hydride used.

In another experiment, the reaction product in oil as such was stirred with absolute ethanol. The oil layer separated out from the alcoholic solution and was removed. The alcoholic solution on treatment with alcoholic solution of potassium hydroxide gave a product which, after washing and drying, gave on assay 94% potassium borohydride. Yield was 25%.

Reaction between sodium hydride and boron phosphate

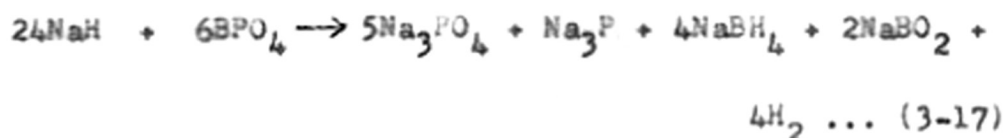
That sodium hydride reacts with boron phosphate to give sodium borohydride as one of the reaction products was reported by Bronaugh in an American patent⁵¹. The author did not investigate the reaction in detail but postulated it to take place according to equation



The patent reports a 5% yield of the borohydride on the basis of the above equation.

Our studies on this reaction have shown that the reaction is not as simple as shown in the above equation. For instance, the reaction product was found to contain sodium phosphide besides sodium borohydride and trisodium phosphate. Our experiment consisted in heating sodium hydride and boron phosphate, mixed in almost stoichiometric proportion according to equation (3-16) above, in inert oil medium at temperature 230°C. and hydrogen pressure of 500 p.s.i. at room temperature, for 24 hours. The reaction product, a greenish yellow mixture, was freed of oil by several washings with petroleum ether, dried and analysed. (Vide Table IA). The presence of sodium borohydride in the reaction product was confirmed by extracting it with anhydrous ethylenediamine; the extracted product, on analysis, gave boron to hydrogen ratio as 1:4.

On the basis of analytical values, the most probable overall reaction may be written as



It appears that the reaction between sodium hydride and BPO_4 first takes place according to equation (3-16) but the products obtained therein further interact partially according to equation



resulting in the final reaction according to equation (3-17).

From the Table IX it can be seen that the values experimentally found and those calculated on the basis of equation (3-17) are comparable except for the values of sodium borohydride and sodium borate, this discrepancy being due to decomposition of some borohydride formed. The difference between the calculated and experimental values of sodium borohydride (this quantity of borohydride maybe considered as decomposed) corresponds to 10.27% NaBO_2 which compares approximately with 9.65% NaBO_2 found in excess over the calculated quantity. The liberation of H_2 in the reaction was indicated by the rise in pressure

in the autoclave observed at the end of the experiment, although the quantity of gas could not be measured under the conditions of work.

Metathesis of the NaBH_4 in the reaction product directly to potassium borohydride was also attempted with part of the reaction product mixture. The mixture was stirred with absolute ethanol and the solution, filtered to remove the insoluble, was treated with an alcoholic solution of potassium hydroxide in slight excess. The precipitate, washed and dried, had 92.7% KBH_4 content; Yield, on the basis of NaBH_4 in the reaction product mixture, was 91%.

II. Studies on the Synthesis of sodium aluminium hydride.

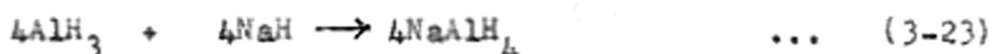
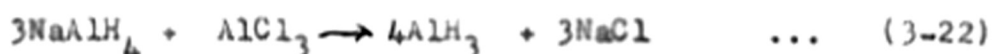
Sodium aluminium hydride was first prepared by Schlesinger and co-workers⁵⁵ by the reaction between sodium hydride and aluminium bromide in a sealed tube at room temperature in the presence of dimethyl ether as solvent. Although a product of satisfactory purity was obtained, the method had several draw-backs, particularly the use of dimethyl ether. Numerous modifications⁵⁶ to this procedure have since been studied. Among the various solvents tested tetrahydrofuran proved superior.

In the course of the above investigation by Schlesinger and others, difficulties were encountered when sodium hydride was reacted with aluminium chloride in tetrahydrofuran. The reaction was slow, as a result of which cleavage of the solvent occurred giving rise not only to decreased yields and purity of end products, but also to the formation of gelatinous deposits which made filtration difficult, sometimes impossible.

The reaction was presumed to take place as follows:



The slowness of the overall reaction was attributed largely to the slowness of reaction (3-19). A method, which appears to avoid this reaction in preparing sodium aluminium hydride, is represented by the following sequence of reactions:-



Both these reactions were found to be rapid in tetrahydrofuran. The sequence gives a nett production of sodium aluminium hydride, since from 3 moles of the compound 4 are theoretically obtainable. The cycle could also be started with some lithium aluminium hydride instead of the sodium compound. However, the cyclic process seems to be only of academic interest, and our attempts to reproduce these reactions were not successful.

The reaction between sodium hydride and aluminium bromide is, however, not too slow. A convenient method of preparing sodium aluminium hydride by reacting sodium hydride and aluminium bromide has been reported by Czech workers⁵⁷.



A recent report on the synthesis of sodium aluminium hydride by direct reaction between sodium, aluminium metal and hydrogen¹⁹, is quite interesting, particularly in view of the low cost it might involve, except for the very high pressure (5000 p.s.i.) that is required.

Synthesis of sodium aluminium hydride was attempted by us by reacting sodium hydride, prepared according to the method described earlier, and aluminium bromide. Although attempts were made essentially under conditions reported by the Czech workers, initial experiments ended up in yielding only some non-reactive polymeric product. The oxidation of bromide in solution to bromine was found to be mainly responsible for this. Utmost precautions against moisture and oxygen led to successful synthesis of the compound. In a typical experiment in which 73 g. sodium hydride was reacted, a solution containing NaAlH_4 , in 32% yield, was obtained.

III. Studies on the reducing action of potassium borohydride on oxyacids of selenium and tellurium.

The alkali borohydrides are known to react with inorganic ions in aqueous solutions by reducing the elements to lower oxidation states, to metals, to borides, or to hydrides.

Elements which have been reported to get reduced to the metals^{58,59} are Hg(II), Pt(IV), Pd(II), Ag(I), Au(III), Pb(II). Schaeffer and co-workers⁶⁰ have developed an analytical scheme for quantitative separations of lead and barium, cadmium and mercury, cadmium and zinc, and lead and zinc, on the basis of reactions of sodium borohydride with these elements. However, no reference exists in the literature on the reaction of borohydrides with compounds containing Se and Te.

Qualitative studies on the reducing action of potassium borohydride on the oxyacids of selenium and tellurium in aqueous solutions led to the following observations:-

(i) SeO_3^{2-} and TeO_3^{2-} are respectively reduced to the metals in acid as well as weakly alkaline solutions.

(ii) SeO_4^{2-} is reduced to SeO_3^{2-} in neutral or alkaline solutions; it is reduced to the metal in acidic solution.

(iii) TeO_4^{2-} is reduced to the metal in both acidic and weakly alkaline solutions.

Reduction of telluric acid to the metal in neutral or weakly alkaline solutions at ordinary temperature was of interest since selenates and tellurates are much more difficult, in neutral or alkaline medium, to reduce to the metal than are the selenites and tellurites. Some reagents known to reduce the hexavalent tellurium to the metal do so only in acid medium, and only hydroxylamine has been reported to reduce the tellurate in a hot ammoniacal solution.

Our experiments have shown that telluric acid can be quantitatively reduced to the metal with potassium borohydride, in weakly alkaline solutions containing potassium chloride. Addition of potassium chloride was found necessary to give a good filtrable precipitate. Complete precipitation of the metal was, however, possible in two stages, over 90% of the metal getting precipitated in the first stage. Results of some of the experiments are given in Table X.

CHAPTER 4 - EXPERIMENTAL

EXPERIMENTAL

I. Preparation of sodium hydride and lithium hydride.

A. Purification of mineral oils.

B.O.C.'s white oil (B.P. > 300°C) and high purity kerosene oil which were used as inert liquids were purified as follows:

4000ml. of the oil was taken in a 5-L capacity aspirator bottle, stirred thoroughly with 200 ml. of conc. H_2SO_4 , and the coloured lower acid layer was separated. The process was repeated five to six times. The oil was then washed, in similar way, with 5% sodium chloride solution, dried over fused calcium chloride and finally over sodium wire for a minimum of 72 hours before use.

B. Dispersion of sodium metal.

The unit for the preparation of sodium dispersion consisted of a Morton creased flask (1-L.cap.) without the bottom indentation, equipped with a Morton high-speed motor-driven stirrer, a Liebig condenser with compressed air as coolant and an oil-filled thermometer-well. (Fig.2). The flask rested on a heating mantle and the motor speed was controlled by a variable auto-transformer. A slow nitrogen purge was started through

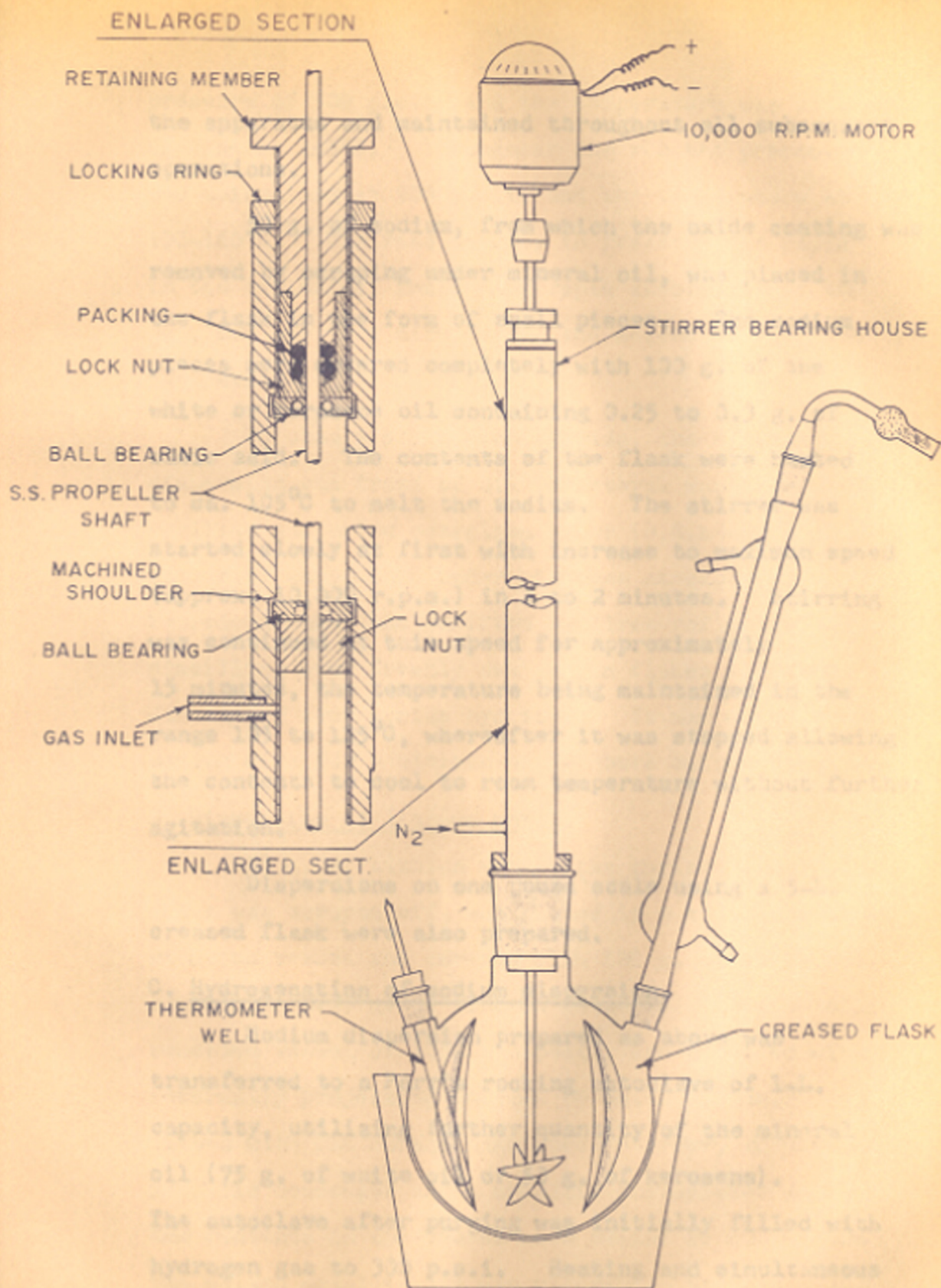


FIG. 2. HIGH SPEED STIRRING APPARATUS

the apparatus and maintained throughout all subsequent operations.

50 g. of sodium, from which the oxide coating was removed by scraping under mineral oil, was placed in the flask in the form of small pieces. The sodium pieces were covered completely with 100 g. of the white or kerosene oil containing 0.25 to 0.3 g. of oleic acid. The contents of the flask were heated to ca. 105°C to melt the sodium. The stirrer was started slowly at first with increase to maximum speed (approx. 10,000 r.p.m.) in 1 to 2 minutes. Stirring was continued at this speed for approximately 15 minutes, the temperature being maintained in the range 105 to 125°C, whereafter it was stopped allowing the contents to cool to room temperature without further agitation.

Dispersions on one pound scale using a 5-L. creased flask were also prepared.

C. Hydrogenation of sodium dispersion.

Sodium dispersion prepared as above was transferred to a Parr's rocking autoclave of 1-L. capacity, utilizing further quantity of the mineral oil (75 g. of white oil or 50 g. of kerosene). The autoclave after purging was initially filled with hydrogen gas to 300 p.s.i. Heating and simultaneous rocking were started. At 130°C when the drop in pressure was observed, more gas was let in to obtain a

pressure of 500 p.s.i. and the temperature was allowed to rise to 160°C. Throughout the run the pressure was maintained at 500 p.s.i. and the temperature at 150-160°C. The rate of drop in pressure was rapid in the beginning, indicating rapid absorption of the gas, and was very slow during the second half of the run period.

To obtain dry sodium hydride, the hydride dispersion was freed of oil by several washings with purified and dried petroleum ether (B.R.40-60°C.) and dried at 50-60°C under nitrogen atmosphere. Petroleum ether was purified by first refluxing and distilling over freshly cut sodium flakes and then distilling over sodium hydride. It was dried over sodium wire for a minimum of 72 hours before use.

B. Dispersion of lithium metal.

25 g. of lithium metal, the surface coating of which was scraped off, was placed in a stainless steel reaction vessel and covered with 100 g. of white oil containing 0.25 g. of lithium stearate. The metallic reaction vessel of 1.5-L. capacity was provided with internally projecting baffles (9 cm. x 1.8 cm.) and fitted with the Morton high speed stirrer, an air-cooled metallic condenser and a metallic thermometer well. The contents in the vessel were heated to 200°C. and the molten metal in oil was vigorously stirred

(7000-8000 r.p.m.) with the high speed stirrer for twenty minutes. Stirring was completely stopped before the contents were allowed to cool. Argon gas was used to provide the inert blanket throughout. A fine dispersion of lithium-metal was obtained.

V. Hydrogenation of lithium dispersion.

The dispersion prepared as in (D) above was hydrogenated in Parr's rocking autoclave at 300-320°C. and 1000 p.s.i. pressure.

F. Analytical.

The determination of completeness of the reaction between sodium and hydrogen to form the hydride presents a problem because of the reactivity of the latter with air and moisture. Sampling is difficult and conventional analytical procedures are inadequate since both sodium and sodium hydride yield hydrogen and caustic when treated with water.

A method was developed based on the differential amounts of hydrogen and caustic formed when sodium hydride containing small amounts of sodium is treated with butyl alcohol and water. Difficulties were felt while using methyl alcohol presumably because of ^{its} high vapour pressure. No weighing was necessary and the dispersions in oil as such could be used.

The method consists in treating an aliquot of sodium dispersion (before hydrogenation) and an aliquot

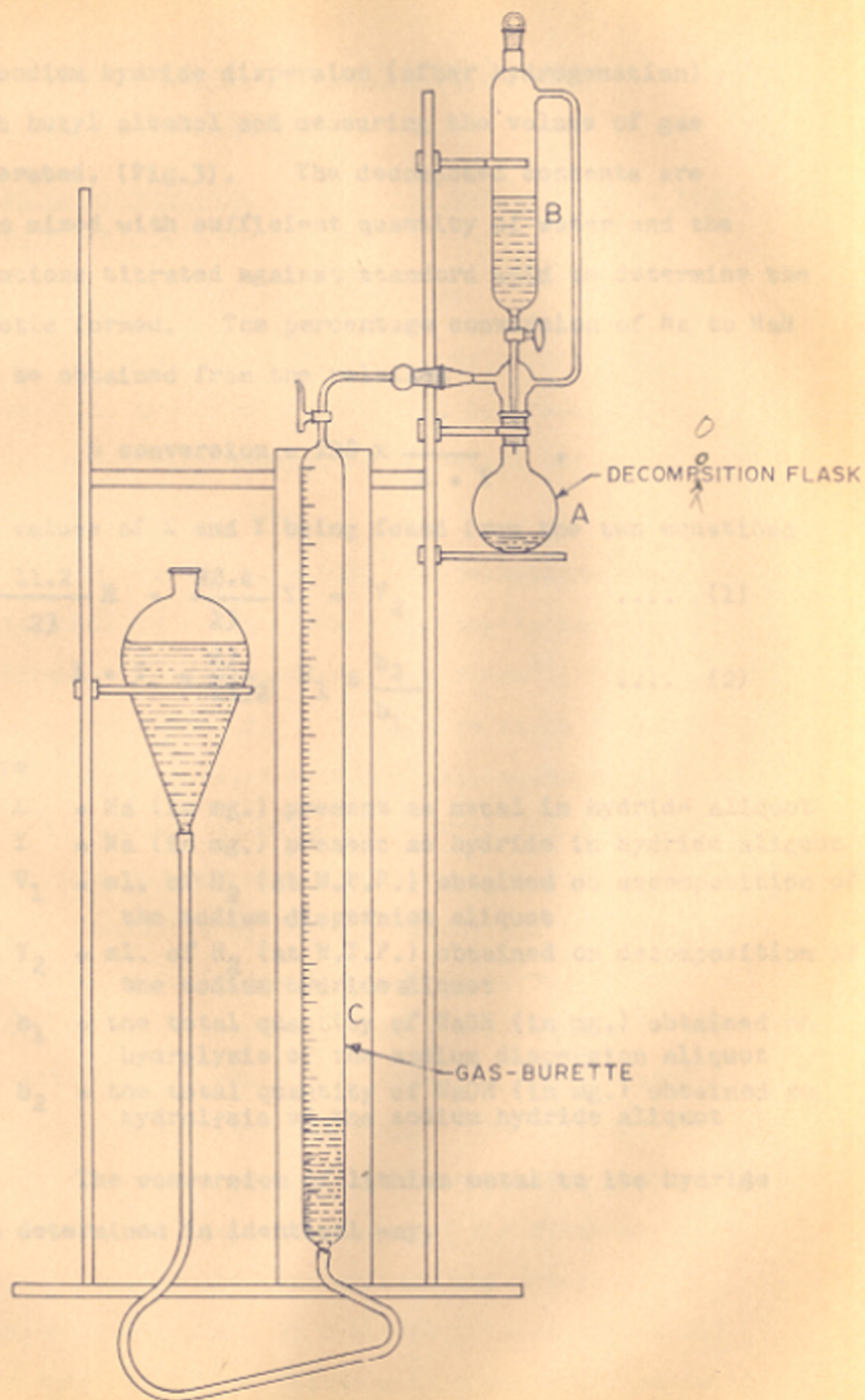


FIG. 3. APPARATUS FOR HYDRIDE ANALYSIS BY HYDROGEN EVOLUTION METHOD

of sodium hydride dispersion (after hydrogenation) with butyl alcohol and measuring the volume of gas liberated. (Fig.3). The decomposed contents are then mixed with sufficient quantity of water and the solutions titrated against standard acid to determine the caustic formed. The percentage conversion of Na to NaH can be obtained from the relation

$$\% \text{ conversion} = 100 \times \frac{Y}{X + Y} ,$$

the values of X and Y being found from the two equations

$$\frac{11.2}{23} X + \frac{22.4}{23} Y = V_2 \quad \dots (1)$$

$$X + Y = \frac{23}{11.2} V_1 \times \frac{b_2}{b_1} \quad \dots (2)$$

where

- X = Na (in mg.) present as metal in hydride aliquot
- Y = Na (in mg.) present as hydride in hydride aliquot
- V₁ = ml. of H₂ (at N.T.P.) obtained on decomposition of the sodium dispersion aliquot
- V₂ = ml. of H₂ (at N.T.P.) obtained on decomposition of the sodium hydride aliquot
- b₁ = the total quantity of NaOH (in mg.) obtained on hydrolysis of the sodium dispersion aliquot
- b₂ = the total quantity of NaOH (in mg.) obtained on hydrolysis of the sodium hydride aliquot

The conversion of lithium metal to its hydride was determined in identical way.

II. Preparation of sodium borohydride and potassium borohydride.

A. Sodium borohydride by reaction between sodium hydride and methyl borate.

A.1. Preparation of methyl borate:

Preparation of methyl borate consisted of two stages: (i) preparation of methyl borate-methanol azeotrope and (ii) separation of methyl borate in pure form from the azeotrope.

Preparation of methyl borate-methanol azeotrope was essentially carried out according to the method described by Schlesinger and co-workers⁶¹, using borax as the boron compound. In a large scale preparation, a 10-L. 3-necked round bottom flask, equipped with a reflux condenser, an oil-seal stirrer and a separating funnel, was charged with a mixture of 5 litres of methanol (purified by fractionation) and 1.25 kg. of commercial borax (containing 60% anhydrous borax). 400 ml. of conc. sulphuric acid (C.P.) placed in the separating funnel was slowly added to the methanol-borax mixture which was kept stirring. The stirrer, reflux condenser, and the separating funnel having been removed subsequently the two side necks of the flask were stoppered and to the central neck was attached a fractionating column, 75 x 4.5 cm., packed with small glass tube pieces and fitted with a condenser as in Fig.4.

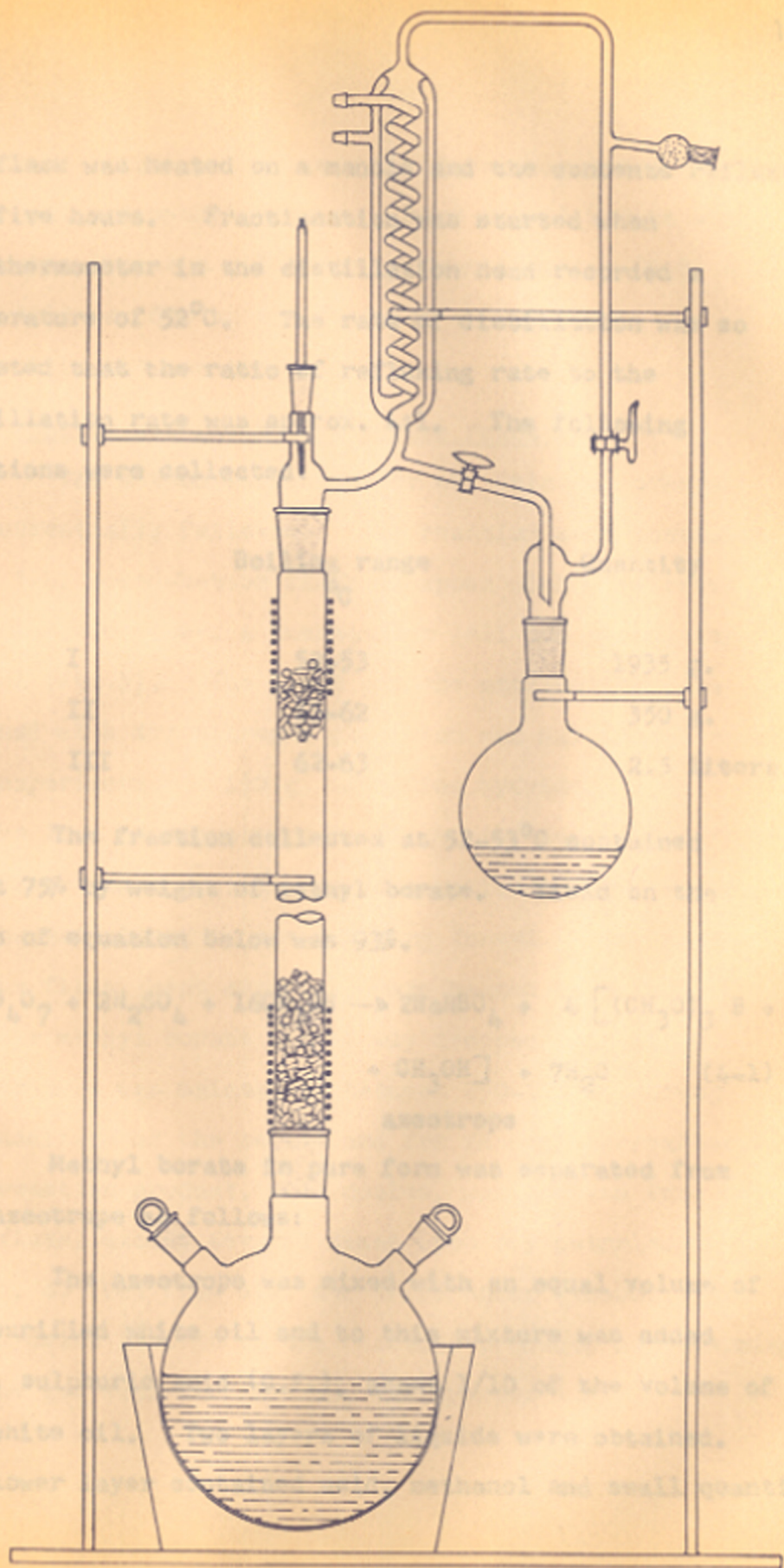
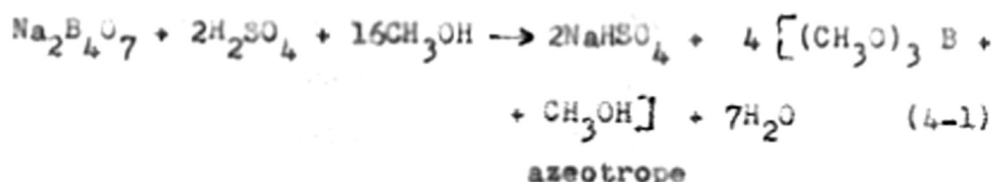


FIG. 4. APPARATUS FOR THE PREPARATION OF ALKYL BORATES.

The flask was heated on a mantle and the contents refluxed for five hours. Fractionation was started when the thermometer in the distillation head recorded a temperature of 52°C. The rate of distillation was so adjusted that the ratio of refluxing rate to the distillation rate was approx. 4:1. The following fractions were collected:

| | Boiling range °C | Quantity |
|-----|---------------------|-------------|
| I | 52-53 | 1935 g. |
| II | 53-62 | 350 g. |
| III | 62-63 | 2.5 liters. |

The fraction collected at 52-53°C contained about 75% by weight of methyl borate. Yield on the basis of equation below was 93%.



Methyl borate in pure form was separated from the azeotrope as follows:

The azeotrope was mixed with an equal volume of dry purified white oil and to this mixture was added conc. sulphuric acid (C.P.), about 1/10 of the volume of the white oil. Two layers of liquids were obtained. The lower layer contained acid, methanol and small quantity

of methyl borate while the upper layer consisted of white oil and methyl borate. Pure methyl borate was separated from the oil layer by fractionation (B.P. 67-68°C). The yield was 65% on the basis of methyl borate content in the azeotrope.

A.2. Sodium hydride-methyl borate reaction:

The method worked out by the Chicago workers was essentially followed. The reaction unit consisted of a 5-L. round-bottom flask equipped with a stirrer, a reflux condenser, a thermometer well and a dropping funnel (Fig.5). The flask and the attachments were flushed with dry nitrogen gas which was maintained throughout the experiment. 150 g. of sodium hydride, in the form of dispersion in white oil, was placed in the flask and a stoichiometric quantity of pure methyl borate was placed in the dropping funnel. The contents in the flask, kept stirring, were heated to 240-250°C and the methyl borate was slowly dropped onto it. Temperature was maintained between 250-260°C. during the addition of the borate and for an hour thereafter. The reaction product, when cooled, was removed from the flask, washed several times with dry petroleum ether, to free from oil, and dried under vacuum. The borohydride content in the reaction product, as determined by the gas evolution method, was approx. 11%.

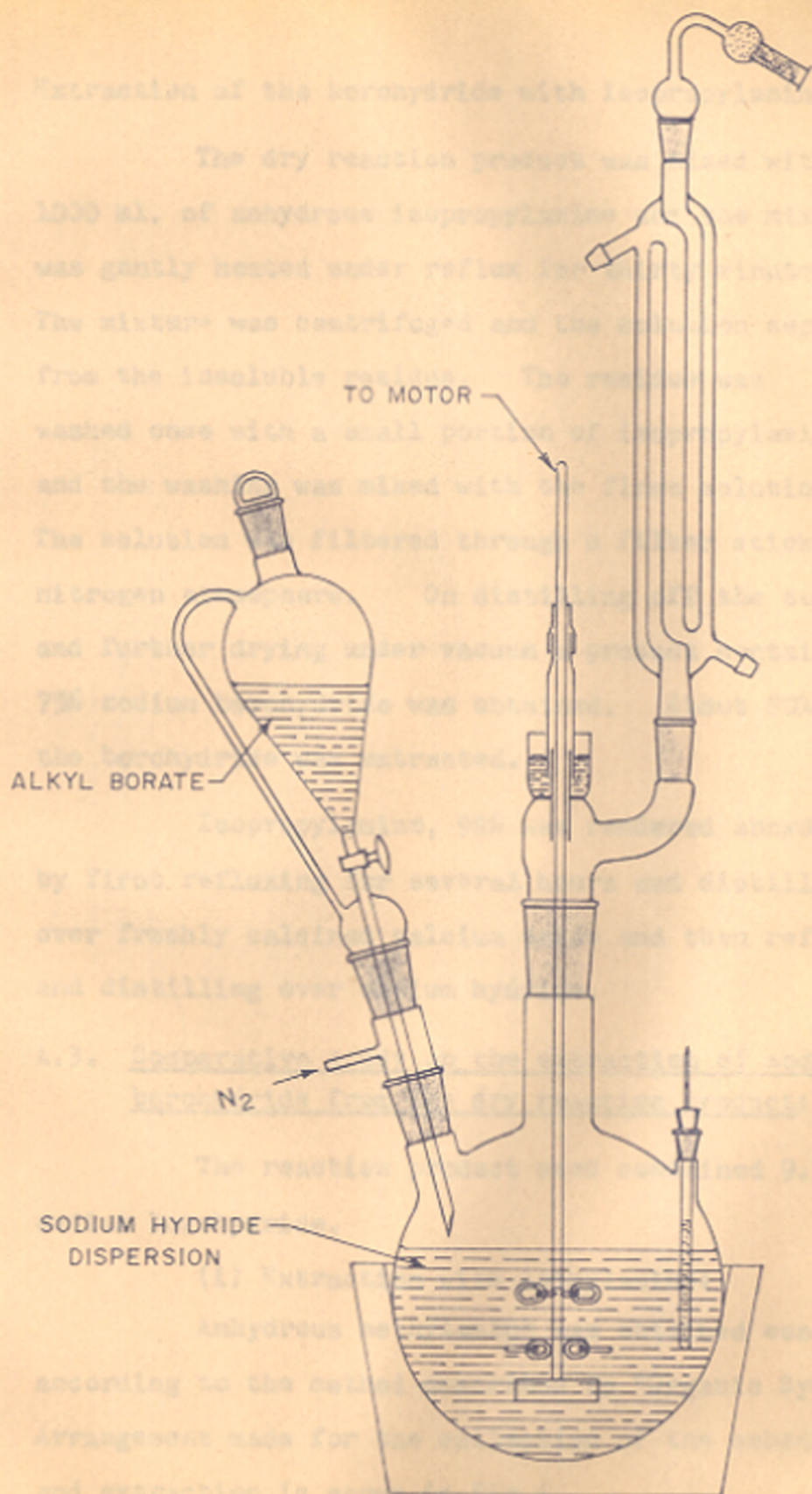


FIG. 5. APPARATUS FOR SODIUM HYDRIDE-ALKYL BORATE REACTION.

Extraction of the borohydride with isopropylamine:

The dry reaction product was mixed with 1000 ml. of anhydrous isopropylamine and the mixture was gently heated under reflux for thirty minutes. The mixture was centrifuged and the solution separated from the insoluble residue. The residue was washed once with a small portion of isopropylamine and the washing was mixed with the first solution. The solution was filtered through a filter stick under nitrogen atmosphere. On distilling off the solvent and further drying under vacuum a product containing 75% sodium borohydride was obtained. About 80% of the borohydride was extracted.

Isopropylamine, 98% was rendered anhydrous by first refluxing for several hours and distilling over freshly calcined calcium oxide and then refluxing and distilling over sodium hydride.

A.3. Comparative study on the extraction of sodium borohydride from the dry reaction product:

The reaction product used contained 9.5% sodium borohydride.

(i) Extraction with methylamine:

Anhydrous methylamine was obtained essentially according to the method described in "Organic Syntheses"⁶². Arrangement made for the collection of the anhydrous solvent and extraction is shown in Fig.6.

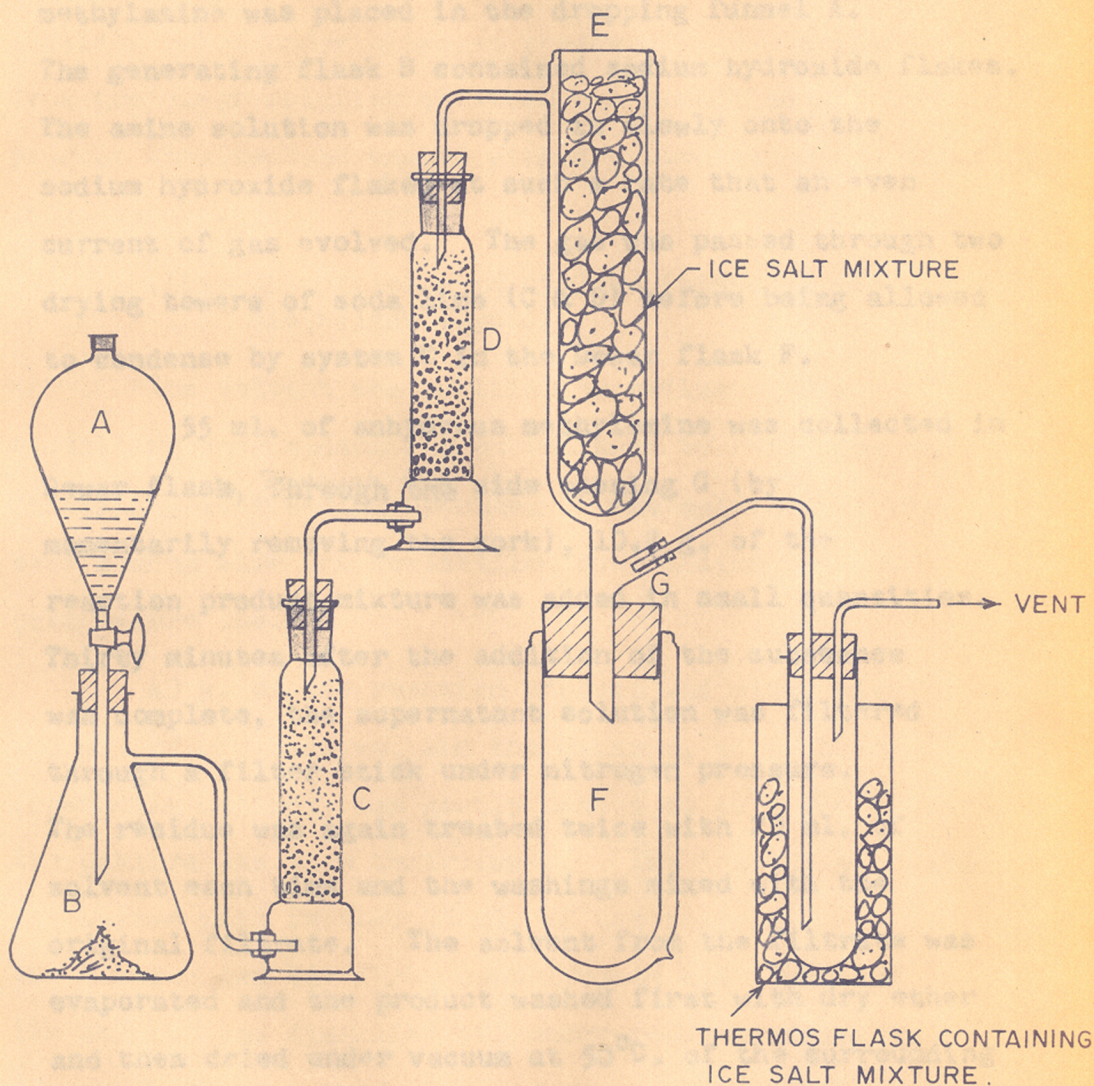


FIG. 6. APPARATUS FOR SODIUM BOROHYDRIDE EXTRACTION WITH METHYLAMINE.

Commercially available aqueous solution of methylamine was placed in the dropping funnel A. The generating flask B contained sodium hydroxide flakes. The amine solution was dropped in slowly onto the sodium hydroxide flakes at such a rate that an even current of gas evolved. The gas was passed through two drying towers of soda lime (C & D) before being allowed to condense by system E in the Dewar flask F.

55 ml. of anhydrous methylamine was collected in Dewar flask. Through the side opening G (by momentarily removing the cork), 10.8 g. of the reaction product mixture was added in small quantities. Thirty minutes after the addition of the substance was complete, the supernatant solution was filtered through a filter stick under nitrogen pressure. The residue was again treated twice with 20 ml. of solvent each time and the washings mixed with the original filtrate. The solvent from the filtrate was evaporated and the product washed first with dry ether and then dried under vacuum at 50°C . of the surrounding bath.

(ii) Extraction with isopropylamine:

Anhydrous isopropylamine was obtained as in (A.2) above. 9 g. of the reaction product was added in small quantities to 50 ml. of anhydrous isopropylamine kept in a Dewar flask and the mixture was mechanically stirred. Any loss of solvent during operation was made

good by the addition of fresh solvent. The solution was separated from the residue by filtering through a filter stick under nitrogen pressure. The solvent from the clear solution obtained was distilled off and the product obtained was washed with dry pure ether and dried under vacuum.

(iii) Extraction with diglyme (dimethyl ether of diethylene glycol):

The solvent was purified by refluxing and distilling over sodium flakes followed by refluxing and distilling over sodium hydride. The solvent was kept over sodium wire and redistilled over sodium hydride just before use.

40 g. of the reaction product was mixed with 100 ml. of dry diglyme, and the mixture, while being constantly stirred, was gently heated to 40°C for 2 hours. The mixture was then centrifuged. The insoluble residue was washed with further 25 ml. of the solvent. The washing and the first centrifugate was mixed and the solvent was distilled off under reduced pressure. The product was washed with dry pure ether and finally dried under vacuum at 60°C. of the surrounding bath.



A.4. Preparation of potassium borohydride by direct metathesis of sodium borohydride contained in the product of reaction between sodium hydride and methyl borate:

In a typical experiment, 140 g. sodium hydride was reacted with methyl borate as in (A.2) above. The reaction product in oil was then slowly added to 3.5 litres of distilled rectified spirit. The liquor obtained consisted of two phases - one of the oil and the other of the alcoholic solution of the borohydride. The latter was separated from the former, filtered and treated with a saturated aqueous solution of 150 g. of potassium hydroxide. The mixture was cooled by surrounding with ice when potassium borohydride precipitated out. The precipitate obtained was recrystallised by dissolving the same in a minimum quantity of cold water and adding to the solution sufficient quantity of rectified spirit. The product obtained was dried under vacuum. 30 g. product containing 95% KBH_4 was obtained.

B. Sodium borohydride by reaction between sodium hydride and isoamyl borate,

B.1. Preparation of isoamyl borate:

Isoamyl borate was prepared by condensing isoamyl alcohol (fractionated from fusel oil, B.R. 128-132°C) with boric acid. A mixture of 168 g. (1.91 mol.) isoamyl alcohol and 31 g. (0.5 mol.) boric acid was placed in a flask rested on a heating mantle. The flask was provided with a fractionating column of about 30 cm. length, packed with small sized-glass tube pieces, to which was connected a condenser as shown in Fig.4. The mixture was gently heated to boiling. The temperature of the vapour at the top of the column remained constant at 92°C for 2 hours while the azeotropic mixture of alcohol and water distilled off. Heating was stopped as the temperature rose to 126°C. The contents of the flask were transferred to another flask and distilled under reduced pressure to obtain the ester, a fraction with B.R. 107-112°C. at 1 mm. pressure. Yield was about 95%.

B.2. Sodium hydride-isoamyl borate reaction:

In this reaction 50 g. sodium hydride in white oil was reacted with stoichiometric quantity of isoamyl borate under conditions same as in (A.2) above. The dry reaction product contained, as determined by the gas evolution method, 7.5% sodium borohydride extraction of which was attempted as follows:

(i) Extraction with isopropylamine:

200 ml. of anhydrous isopropylamine was distilled over NaH directly into a round bottom flask flushed with nitrogen, containing 50 g. of the dry reaction product. The slurry was stirred for half an hour as the solvent was allowed to reflux with gentle heating. The solution was filtered through a filter stick under N_2 pressure. On distilling off most of the solvent at ordinary pressure, the product was finally dried under vacuum at $50-60^{\circ}C$ of the surrounding bath.

(ii) Extraction with methylamine:

For the collection of methylamine an arrangement as in (A.3) above was set up. The Dewar flask was replaced by a tube of suitable width and length which was surrounded by an ice and salt freezing mixture (-10 to $-15^{\circ}C$). After collecting 60 ml. of methylamine in the tube, 25 g. of the reaction product was slowly added and the mixture was mechanically stirred. The solution was then filtered through a filter stick under nitrogen pressure. The solvent was evaporated and the product dried under vacuum at $50^{\circ}C$ of the surrounding bath.

B.3. Preparation of potassium borohydride by direct metathesis of sodium borohydride contained in the product of reaction of sodium hydride and isoamyl borate:

(i) 72 g. of the dry reaction product obtained in (2) above was dissolved in 300 ml. of ice-cooled absolute ethanol. The solution was filtered and mixed with a 10% solution (in absolute alcohol) of 12 g. potassium hydroxide (C.P. 85% pure) and the mixture was allowed to stand for several hours. The precipitate was collected in centrifuge tubes and washed five times with small portions of absolute alcohol. It was then dried under vacuum at 60-70°C of the surrounding bath. A product (5.2 g.) containing 98.9% KBH_4 , with boron to hydrogen ratio of 1:4, was obtained. Yield was approx. 50% on the basis of sodium hydride used.

(ii) 50 g. sodium hydride was reacted with isoamyl borate as in (B.2) above. Although sufficient additional quantity of white oil was added, the reaction product, when cooled, was in the form of pasty mass. It was dissolved in 400 ml. of ice-cooled absolute ethanol to give a liquor consisting of two phases, one of the oil and the other of the alcoholic solution of the borohydride. The borohydride solution, separated from the oil, was treated with a 20% alcoholic

solution of 35 g. KOH (C.P., 85% pure) and the mixture was allowed to stand for ten hours. The precipitate was collected in centrifuge tubes, washed 5-6 times with small portions of absolute alcohol and dried under vacuum at 60-70°C of the surrounding bath. The product (7 g.) contained 94% KBH_4 . Absolute alcohol used was purified by refluxing and distilling over quick-lime.

C. Sodium borohydride by reaction between sodium hydride and boron phosphate.

C.1. Preparation of boron phosphate:

Boron phosphate, BPO_4 , was prepared by calcination of an intimate mixture of boric acid (A.R.) and diammonium hydrogen phosphate (A.R.) in stoichiometric proportions at 800°C. for 4 hours⁶³. (B - found 10.41%, calcd. 10.38%).

C.2. Sodium hydride-boron phosphate reaction:

A slurry of 34 g. sodium hydride (90% pure) and 35 g. boron phosphate in 200 ml. of the white oil was introduced in Parr's rocking type autoclave of one litre capacity. The autoclave was filled with H_2 gas to a pressure of 500 p.s.i. at room temperature. Heating and rocking were simultaneously started. The temperature was allowed to rise to 230°C at which the pressure indicated was 1500 p.s.i. and under these conditions the reaction was carried out for two and

half hours. On cooling the autoclave to room temperature, an increase of pressure in the autoclave was observed. The product obtained was freed of oil by several washings with dry petroleum ether (B.R.40-60°C) and dried under vacuum. The reaction product weighed 65 g. and contained about 6% sodium borohydride.

C.3. Extraction of the sodium borohydride from the reaction product:

34 g. of the reaction product was vigorously stirred with 90 ml. of anhydrous ethylene-diamine at 75-80°C. for twenty minutes and the mixture was centrifuged. Ethylenediamine from the centrifugate was distilled off under reduced pressure and the residue was dried under vacuum at 50°C of the surrounding bath. 1.95 g. of a product containing 51.12% sodium borohydride was obtained. Boron to hydrogen ratio in the product was 1:4.

D. Analytical.

Sodium and potassium borohydrides were determined either by the gas evolution method or by iodometric method.

The gas evolution method is based on the principle that the borohydride upon the addition of acid evolves hydrogen according to the equation



The apparatus that was set up for the gasometric analysis is shown in Fig. 3. A known weight of the sample was taken in flask A, treated dropwise with dilute acid (HCl or H₂SO₄) from the funnel B and the gas liberated was measured in the gas-burette C.

$$\% \text{NaBH}_4 = \frac{X \times 37.3 \times 100}{89.6 \times S}$$

$$\% \text{KBH}_4 = \frac{X \times 53.92 \times 100}{89.6 \times S}$$

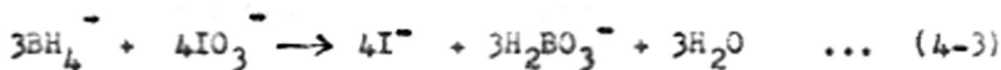
where

X = ml. of gas liberated (at N.T.P.)

S = sample weight in mg.

Whenever presence of any sodium hydride was suspected, the sample was previously wetted with alkaline water.

The iodometric method consists of oxidizing the borohydride with excess potassium iodate and determining the excess iodate by the usual iodometric procedure⁶⁴.



In the procedure, a sample of known weight (containing 20 mg. of sodium borohydride or 30 mg. of potassium borohydride) was transferred to a 250 ml. iodine flask and dissolved in 5 ml. of 1N NaOH. (In case of a solution of the borohydride, a suitable aliquot to give the desired weight was taken). To this was added 35.00 ml.

of standard (0.25 N) potassium iodate solution and mixed thoroughly. 2 grams of potassium iodide were added and mixed, followed by 10 ml. of 4N sulphuric acid. The flask was placed in a dark place for 2 to 3 minutes and then the liberated iodine was titrated with standard (0.1N) thiosulphate solution, using the starch indicator.

$$\% \text{ NaBH}_4 = \frac{(XN_1 - YN_2) \times 0.473}{S}$$

$$\% \text{ KBH}_4 = \frac{(XN_1 - YN_2) \times 0.674}{S}$$

where

- X = ml. of potassium iodate
- N₁ = normality of potassium iodate
- Y = ml. of sodium thiosulphate
- N₂ = normality of sodium thiosulphate
- S = sample weight in grams.

Boron in the sample was determined by the conventional acid-base titration method using mannitol. A known weight of the sample (containing about 70 mg. of the borohydride salt) was taken, dissolved in sufficient quantity of distilled water, and the solution was titrated with standard (0.1N) HCl to the methyl red end point. To the solution was added 0.5 ml. of approx.

6N HCl. The solution was heated to simmering for sometime to expel CO_2 . When cooled, 0.5N NaOH was added to obtain the first yellow colour of the indicator. Mannitol was added and the boric acid was titrated with standard (0.1N) NaOH to the phenolphthalein end point.

Boron in the product of reaction between sodium hydride and boron phosphate was determined by methyl borate method⁶⁵ as follows:

A known weight of the product (0.5 to 0.6 g.) was taken in a solution with 5 ml. of 6N-hydrochloric acid and the solution was placed in flask B shown in Fig.7. Anhydrous calcium chloride was added (1. g. per ml.) to the solution. Flask A contained methyl alcohol which was distilled. When about 25 ml. of alcohol condensed in B, the latter was heated so that the volume of liquid in B remained almost constant. About 100 ml. of liquid were collected in flask C which was thereafter quickly replaced with another to collect more of the distillate. To the first 100-ml. fraction was added several drops of methyl red and the solution titrated against standard (0.1N) NaOH. Few drops of phenolphthalein were added and the titration was carried further to this end-point. This procedure was repeated on the second 100 ml. fraction and so on till not more than 0.1 ml. of 0.1N NaOH was used between the two end points.

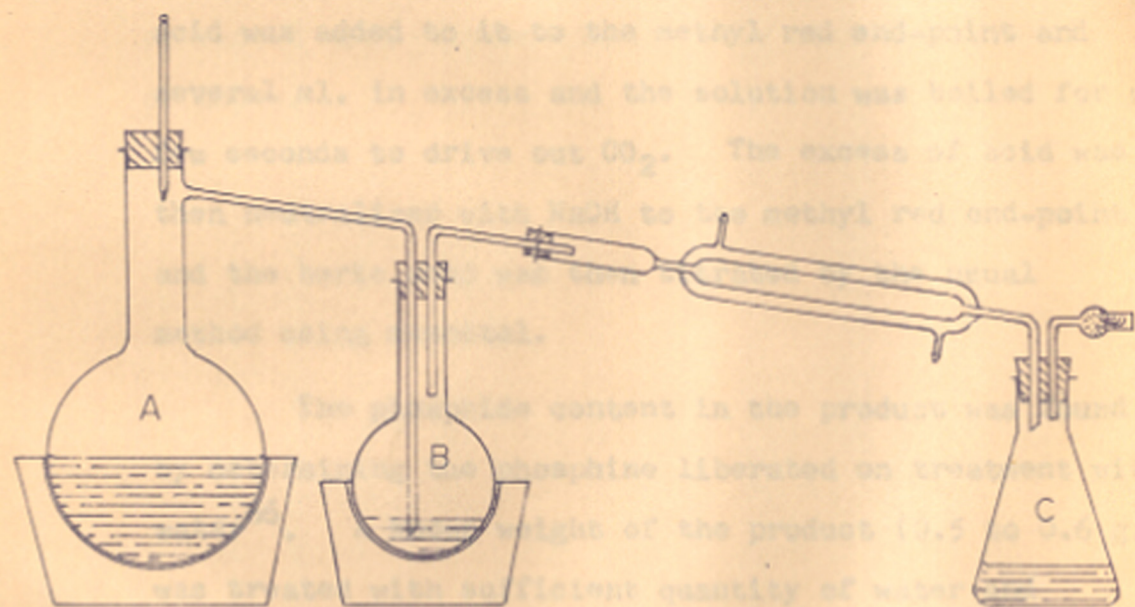
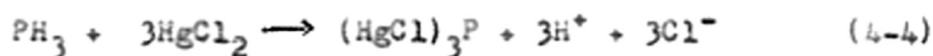


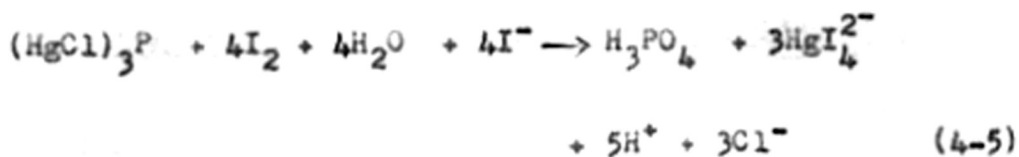
FIG. 7. APPARATUS FOR BORON DETERMINATION BY METHYL BORATE METHOD.

To each fraction further NaOH was added in a volume double that used between the two end points. All the fractions were combined and treated on a water bath to drive off methyl alcohol. The solution was transferred to an evaporating dish and concentrated to 25 ml. on a water bath. The concentrated solution was transferred back to a titration flask, hydrochloric acid was added to it to the methyl red end-point and several ml. in excess and the solution was boiled for a few seconds to drive out CO₂. The excess of acid was then neutralized with NaOH to the methyl red end-point and the boric acid was then titrated by the usual method using mannitol.

The phosphide content in the product was found by determining the phosphine liberated on treatment with water⁶⁶. A known weight of the product (0.5 to 0.6 g.) was treated with sufficient quantity of water and phosphine liberated was, by a current of nitrogen, swept through and absorbed in 50 ml. of 10% mercuric chloride solution.



(HgCl)₃P formed was determined by treating it with excess of standard (0.1N) iodine solution in presence of potassium iodide and back-titrating the excess iodine with standard (0.1N) sodium thiosulphate solution.



The phosphate content was determined as $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, by the known gravimetric procedure.

Boron and phosphide content in the product extracted with ethylenediamine were also determined as above.

III. Preparation of sodium aluminium hydride.

A. Purification of solvents.

Tetrahydrofuran:

Tetrahydrofuran was first shaken with and refluxed over potassium hydroxide pellets. The solvent was next refluxed over freshly cut sodium flakes, followed by refluxing and distillation over sodium hydride. The distilled solvent was first dried over sodium wire and kept over Na-K alloy for a minimum of 48 hours before being finally redistilled over sodium hydride directly into the reaction flask during the experiment.

Benzene:

Benzene was treated with conc. H_2SO_4 , in the same way as the mineral oils in (I.A) above, till the acidic layer became almost colourless. The solvent was then washed several times with distilled water, dried first over fused calcium chloride, then over sodium wire and finally over sodium-potassium alloy.

B. Preparation of aluminium bromide.

Aluminium bromide was prepared essentially according to the method described in Inorganic Syntheses⁶⁷. 100 g. aluminium turnings, degreased by treatment with petroleum ether and dried at $110^\circ C$, was placed in a

three-necked round-bottom reaction flask. A tall and wide air condenser with calcium chloride guard tube was connected to the central neck of the reaction flask, a dropping funnel (with a long stem almost touching the turnings inside the flask) to one of the side necks and a nitrogen inlet to the third neck. 125 ml. of bromine was placed in the dropping funnel. The flask was first flushed with dry nitrogen gas and then heated on a burner to approx. 100°C. Heating was stopped and bromine was added drop by drop onto the metal. Initially, and throughout the run, some sparking and flashing was observed inside the flask. After all the bromine was added, the external heat was applied again and the aluminium bromide formed was refluxed until the liquid returning down the condenser wall was colourless. 250 g. of very pure aluminium bromide (60% yield) was obtained by two distillations, under nitrogen atmosphere, of the product formed.

C. Sodium hydride-aluminium bromide reaction.

The reaction unit assembly is shown in fig. 8. Nitrogen gas, used to provide inert atmosphere, was passed through a series of towers containing KOH, P₂O₅, Mg(ClO₄)₂ and finally bubbled through liquid Na-K alloy.

The unit was flushed with nitrogen and 73 g. sodium hydride (dry powder of 90% purity) was placed in the flask B. 400 ml. of previously purified and dried

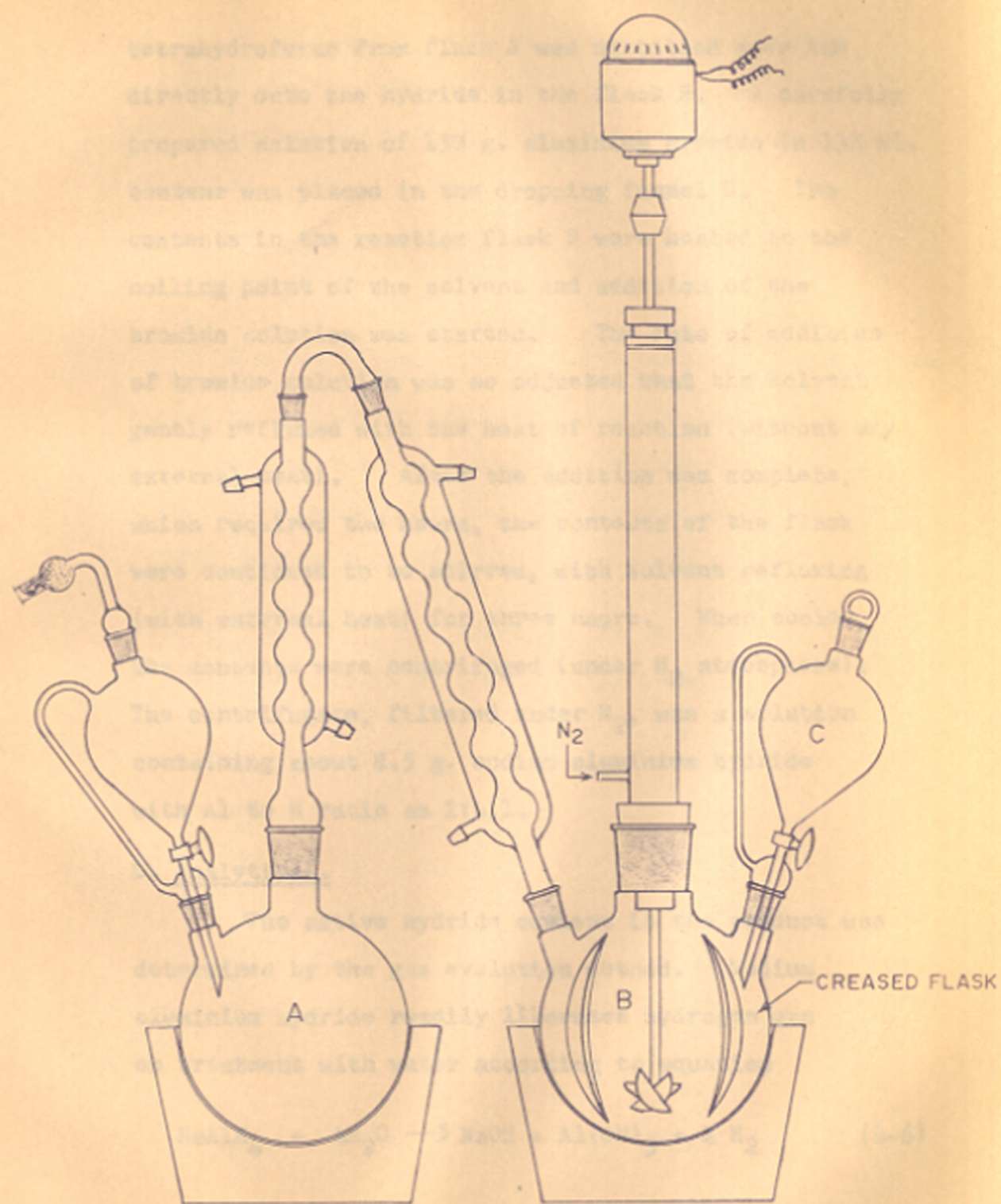


FIG. 8. APPARATUS FOR THE PREPARATION OF SODIUM ALUMINIUM HYDRIDE.

tetrahydrofuran from flask A was distilled over NaH directly onto the hydride in the flask B. A carefully prepared solution of 130 g. aluminium bromide in 130 ml. benzene was placed in the dropping funnel C. The contents in the reaction flask B were heated to the boiling point of the solvent and addition of the bromide solution was started. The rate of addition of bromide solution was so adjusted that the solvent gently refluxed with the heat of reaction (without any external heat). After the addition was complete, which required two hours, the contents of the flask were continued to be stirred, with solvent refluxing (with external heat) for three hours. When cooled, the contents were centrifuged (under N₂ atmosphere). The centrifugate, filtered under N₂, was a solution containing about 8.5 g. sodium aluminium hydride with Al to H ratio as 1:4.1.

D. Analytical.

The active hydride content in the product was determined by the gas evolution method. Sodium aluminium hydride readily liberates hydrogen gas on treatment with water according to equation



A suitable aliquot of the solution of the compound was treated dropwise with water and the gas liberated was collected by downward displacement of water.

$$\text{NaAlH}_4 = \frac{\bar{x} \times 53.97}{89.6} \text{ mg.}$$

\bar{x} = ml. of gas (at N.T.P.) liberated on hydrolysis.

Aluminium content in solution was determined by precipitating the element with 8-hydroxyquinoline from the decomposed aliquot after decomposing the organic matter with $\text{HNO}_3 + \text{H}_2\text{SO}_4$ mixture.

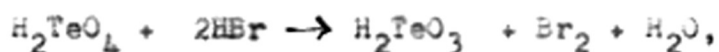
(NaAlH_4 found in 3 ml. aliquot = 78.94 mg;

Al-found = 38.35 mg., calc. = 39.47 mg.)

IV. Reduction of telluric acid with potassium borohydride.

A. Preparation of standard telluric acid solution:

About 3 g. of telluric acid (A.R., B.D.H.) was dissolved in distilled water and the solution was made up to 500 ml. in a standard flask. Tellurium content of the solution was determined volumetrically⁶⁸ by reduction of telluric acid with excess hydrobormic acid



absorption of the bromine in potassium iodide solution and titration of the iodine liberated against standard sodium thiosulphate.

B. Reduction of telluric acid with KBH_4 :

10 ml. of the telluric acid solution was pipetted into a tall beaker and to this was added 25 ml. of 1.5% KCl solution. The solution (pH between 5 and 6) was kept stirring with a magnetic stirrer and solid potassium borohydride (98% pure) was added in small quantities till most of the tellurium was precipitated. The black precipitate was collected on weighed sintered crucible, washed several times with cold water, then thrice with small quantities of absolute alcohol and finally dried at 105°C and weighed. The filtrate and washings were mixed and the solution (pH ≈ 9),

concentrated to 25 ml, was again treated with further quantities of potassium borohydride till rest of tellurium was completely precipitated. This precipitate was also collected on a sintered crucible, washed with cold water and absolute alcohol as above and dried at 105°C. About 0.25 g. of the potassium borohydride was required for complete precipitation of the tellurium. Complete precipitation of the element could not be effected in a single step.

TABLES I-X

Table I

Relation of Periodic Table to Hydride-Forming Ability

| Saline Hydrides | Molecular and Polymeric Hydrides (non-metals omitted) | Metallic Hydrides | Unspecified Types |
|------------------------|-----------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------|-----------------------------------|
| LiH | (BH ₃) ₂ (etc.) | | |
| BeH ₂ | | | |
| NaH | (AlH ₃) _n SiH ₄ (etc.) | ScH ₂ TiH ₂ VH _{2,3,1.6} (CrH > 1) Mn Fe Co NiH ₂ (?) | (CuH) (ZnH ₂) |
| MgH ₂ | | | |
| KH | GeH ₃ (?) GeH ₂ AsH ₃ (etc.) | YH _{2,3} ZrH ₂ NbH _{1,2} Mo | Ag (CdH ₂) |
| CaH ₂ | | | |
| RbH | InH ₃ ? | LaH _{2,3} HfH ₂ TaH<1 W | Au (HgH ₂) |
| SrH ₂ | SnH ₄ SbH ₃ TeH ₂ | | |
| BaH ₂ | Tl (PbH ₄) BiH ₃ PoH ₂ | | |
| Lanthanides (Metallic) | LaH _{2,3} CeH _{2,3} PrH _{2,3} NdH _{2,3} | Pm SmH _{2,3} EuH ₂ GdH _{2,3} TbH ₂ Dy Ho Er Tm | YbH ₂ LuH ₂ |
| Actinides (Metallic) | AcH ₂ ThH _{2,3,75} PaH ₂ UH ₃ | Np PuH ₃ AmH ₂ Cm | Cf Fm Mv |

Known hydrides are formulated. Those known to be thermally unstable under ordinary conditions are in parentheses.

Table II

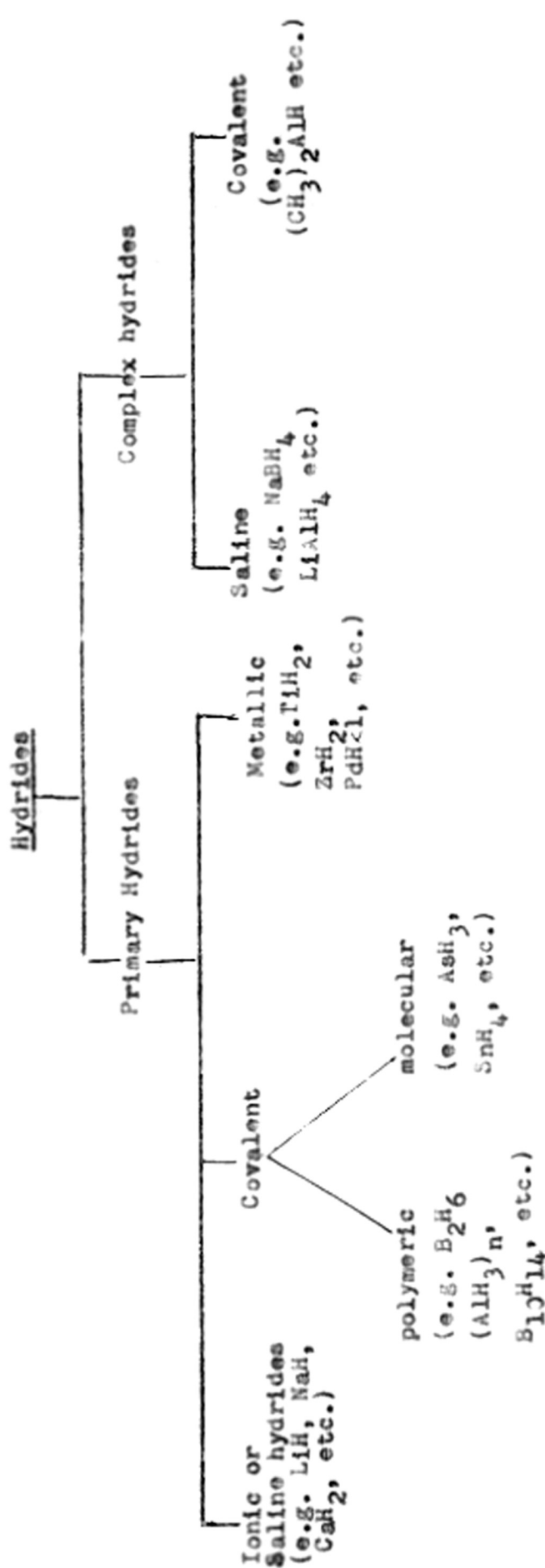
Classification of Hydrides

Table III

Functional Groups Reduced by Lithium Aluminium Hydride.

| <u>Functional Group</u> | <u>Product</u> |
|--------------------------------------|----------------------------|
| <u>A. Oxygen-containing groups</u> | |
| Aldehyde | Primary alcohol |
| Ketone | Secondary alcohol |
| Quinone | Hydroquinone |
| Carboxylic acid | Primary alcohol |
| Acid anhydride | Primary alcohol |
| Acyl halide | Primary alcohol |
| Ester | Primary alcohol |
| Lactone | Diol |
| Epoxide | Alcohol |
| Orthoester | Acetal |
| Hydroperoxide | Alcohol |
| Peroxide | Alcohol |
| Ozonide | Alcohol |
| <u>B. Nitrogen-containing groups</u> | |
| Amide | |
| Unsubstituted | Primary amine |
| Monosubstituted | Secondary amine |
| Disubstituted | Tertiary amine or aldehyde |
| Lactam | Cyclic amine |
| Imide | Cyclic amine |
| Carbamate | Amine + alcohol |
| Nitrile | Primary amine or aldehyde |
| Isocyanide | Secondary amine |
| Oxime | Amine |
| Isocyanate | Secondary amine |
| Nitrogen oxide | Amine |

(Table III continued)

| <u>Functional group</u> | <u>Product</u> |
|--------------------------|----------------|
| C-nitroso-compound | Amine |
| Nitrosamine | Hydrazine |
| Nitro, alkyl | Primary amine |
| Nitro, aryl | Azo compound |
| Hydroxylamine | Amine |
| Azoxy compound | Azo compound |
| Azide | Amine |
| Diazo compound | Amine |
| Quarternary salt, cyclic | o-Dihydroamine |

C. Sulphur-containing groups

| | |
|--------------------|-------------------------------|
| Dithiol | Mercaptan |
| Disulfide | Mercaptan |
| Trisulfide | Mercaptan |
| Tetrasulfide | Mercaptan |
| Episulfide | Mercaptan |
| Sulfoxide | Sulfide |
| Sulfone | Sulfide |
| Sulfonic anhydride | Sulfinic acid or Mercaptan |
| Sulfonyl halide | Mercaptan |
| Sulfonic ester | |
| Alkyl | Hydrocarbon |
| Aryl | Phenol |
| Sulfinic acid | Disulfide + Mercaptan |
| Sulfenyl halide | Disulfide |
| Thioester | Alcohol |
| Thioamide | Amine + nitrile |
| Thiocyanate | Mercaptan |
| Isothiocyanate | Amine |

D. Halogen-containing groups

| | |
|--------------|--------|
| Alkyl halide | Alkane |
|--------------|--------|

Table IV
Reductions with Sodium Borohydride

| Functional groups reduced Functional group | Product | Functional group normally not reduced |
|-----------------------------------------------|--------------------------|------------------------------------------|
| Aldehyde | Primary alcohol | Carboxylic acid |
| Ketone | Secondary " | Anhydride |
| Acid chloride | Primary alcohol | Ester |
| Lactone | Dialcohol | Amide |
| Hydroperoxide | Alcohol | Imide |
| Quaternary ammonium salt | O-Dihydro derivatives | Acetal |
| Sulfoxide | Mercaptan | Nitrile, |
| | | Nitro, aromatic |
| | | Halide |
| | | Double bond |

Table V
Borohydride Metathesis

| BH_4^- | Salt | Solvent | Product |
|-----------------|-----------------------------|------------------|-------------------------------|
| NaBH_4 | LiCl | Isopropylamine | LiBH_4 |
| KBH_4 | LiCl | Tetrahydrofuran | LiBH_4 |
| NaBH_4 | CaCl_2 | THF or methanol | $\text{Ca}(\text{BH}_4)_2$ |
| NaBH_4 | KOH | Water | KBH_4 |
| NaBH_4 | $(\text{CH}_3)_4\text{NOH}$ | Water or alcohol | $(\text{CH}_3)_4\text{NBH}_4$ |
| NaBH_4 | AlCl_3 | None | $\text{Al}(\text{BH}_4)_3$ |

Table VI
Hydrogenation of Sodium Dispersion

| Expt. No. | Mineral oil used | Hydrogenation period (hrs.) | Conversion of metal to hydride (%) | Nature of the product |
|-----------|------------------|-----------------------------|------------------------------------|-----------------------|
| 1 | White oil | 4 | 83.5 | white |
| 2 | White oil | 7 | 96 | -do- |
| 3 | Kerosene oil | 9 | 99 | -do- |
| 4 | White oil | 12 | 97 | -do- |
| 5 | White oil | 13 | 99 | -do- |
| 6 | Kerosene oil | 7 | 98 | -do- |

Table VII

Extraction of Sodium Borohydride from
Sodium Hydride-Methyl Borate Reaction Product

| Solvent used | Wt. of reaction* product taken (g) | Wt. of the extracted product (g) | NaBH ₄ content in the extracted product (%) |
|--------------------|------------------------------------------|-------------------------------------------|-----------------------------------------------------------------|
| 1. Isopropyl amine | 9.00 | 0.70 | 71 |
| 2. Diglyme | 40.00 | 1.70 | 76 |
| 3. Methylamine | 10.80 | 1.11 | 55 |

*The reaction product contained 9.5% NaBH₄.

Table VIII

Extraction of Sodium Borohydride from
Sodium Hydride-Isoamyl Borate Reaction Product

| Solvent used | Wt. of reaction product taken* (g) | Wt. of the extracted product (g) | NaBH ₄ content in the extracted product (%) |
|---------------------|---------------------------------------------------------------------|-------------------------------------------|-----------------------------------------------------------------|
| 1. Isopropyl amine | 50 | 22 | 10.8 |
| 2. Methylamine | 25 | 10 | 11.2 |
| 3. Ethylene-diamine | The entire mixture was highly soluble in these solvents. | | |
| 4. Diglyme | | | |

*The reaction product contained 7.5% NaBH₄.

Table IX

Analytical Data of the
Sodium Hydride-Boron Phosphate Reaction Product

| | Calcd. %* | Found % [Ⓔ] |
|---------------------------------|-----------|----------------------|
| Na ₃ PO ₄ | 68.11 | 66.55 |
| Na ₃ P | 8.31 | 8.51 |
| B | 5.39 | 5.38 |
| NaBH ₄ | 12.63 | 6.72 |
| NaBO ₂ | 10.96 | 20.61** |

* The values have been calculated according to equation (3-17)[†] on the basis of the total weight of the solid reaction product.

Ⓔ The values have been calculated on the basis of the weight of the reaction product mixture less the weight of the small quantities of unreacted starting materials and impurities.

** Value calculated from total B less boron present in NaBH₄.

† pp. 31

Table X
 Reducing Action of Potassium Borohydride
 on Telluric Acid

| Expt. | Qty. of Te in solution (mg.) | Wt. of Te obtained | | |
|-------|------------------------------------|--------------------|--------------------|----------------|
| | | 1st stage (mg.) | 2nd stage (mg.) | Total (mg.) |
| 1 | 34.4 | 33.15 | 1.4 | 34.55 |
| 2 | 34.4 | 31.8 | 1.8 | 33.6 |
| 3 | 34.4 | 30.8 | 3.55 | 34.35 * |
| 4 | 34.4 | 32.25 | 3.0 | 35.25 |

* The precipitation was carried out in presence of 28 mg.
 Se as SeO_4^{2-} .

SUMMARY

S U M M A R Y

The very selective nature of reduction of many organic compounds with complex hydrides, especially the borohydrides, has recently gained considerable importance in synthetic organic chemistry. Yet the preparation of these inorganic hydrides has remained a difficult problem of inorganic synthesis. This thesis deals mainly with the synthetic studies on some of the important alkali metal hydrides, namely, sodium hydride and lithium hydride from among the simple hydrides and sodium borohydride, potassium borohydride and sodium aluminium hydride among the complex hydrides.

Chapter 1 gives an introduction to the "family of hydrides" and the classification, properties and uses of the hydrides in general. Handling of the alkali metal hydrides, which is of considerable importance owing to the high reactive nature of these compounds, has also been discussed in this chapter.

Sodium hydride, the key chemical in the preparation of complex hydrides, poses a problem of

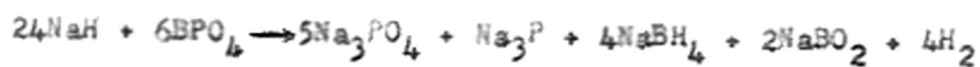
material handling on account of its spontaneous ignition in moist air. Its synthesis was studied and conditions ^{have been} ~~were~~ worked out for an almost quantitative conversion of sodium metal to its hydride. These experimental results are reported in chapter 2 after a brief review of the background literature. Preparation of lithium hydride is also reported in the same chapter.

Studies were carried out on the synthesis of sodium borohydride, potassium borohydride and sodium aluminium hydride using the sodium hydride prepared according to method described in chapter 2. These studies are reported in chapter 3 after a summary of earlier work.

Section I of chapter 3 is concerned with the synthesis of borohydrides. Sodium borohydride was prepared by the reaction between sodium hydride and methyl borate and subsequent extraction of the compound with anhydrous isopropylamine. Potassium borohydride was also prepared from this reaction mixture. A comparative study was made on the extraction of sodium borohydride from the reaction mixture with solvents like isopropylamine, methylamine and diglyme (dimethyl ether of diethylene glycol).

To utilize indigenous resources for preparing sodium borohydride, the reaction between sodium hydride and isocamyl borate (prepared from fusel oil, a waste product of India's distilleries) was studied. Usual solvents isopropylamine, methylamine, ethylenediamine and diglyme failed to extract the sodium borohydride in good purity from this reaction product. However, it could be easily converted to potassium borohydride of very high purity.

The reaction between sodium hydride and boron phosphate was found to be more complex than originally thought to be. Besides Na_3PO_4 , sodium phosphide, Na_3P , was also formed (detected for the first time by the odour of phosphine). Studies on this reaction suggest that the reaction takes place, perhaps, according to the following overall equation:



Sodium borohydride from the above reaction product was extracted with anhydrous ethylenediamine. Potassium borohydride could also be obtained by reacting the above mixture with potassium hydroxide.

Sodium aluminium hydride was prepared (described in section II of chapter 3) by reaction between sodium hydride in tetrahydrofuran suspension and aluminium bromide in benzene solution, with strict exclusion of moisture and oxygen.

Qualitative studies showed that potassium borohydride reduced selenite, tellurite and tellurate ions to the corresponding metals in acidic as well as weakly alkaline solutions. Telluric acid was quantitatively reduced to tellurium metal in weakly alkaline solution. These observations are reported in section III of chapter 3.

Chapter 4 gives details of the experiments carried out. All Tables of data have been given at the end.

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