# THE CHEMISTRY OF COMPLEX ALUMINOHYDRIDES

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## I. Introduction

Applications of complex metal hydrides in organic synthesis have been found to be both unusually selective and numerous; thus the importance of these compounds cannot be overemphasized. Excellent treatises are available describing applications of these reagents in organic synthesis; however, little is known about the actual reagents and their behavior toward inorganic compounds. Nöth (*79*) at the Institute for Inorganic Chemistry in Munich has published an excellent summary dealing with the inorganic chemistry of complex borohydrides. The present contribution is meant to cover the preparations and inorganic chemistry of the complex aluminohydrides in an attempt to fulfill a long standing need to organize and review this important area of chemistry. Over 300 references have been reviewed covering the years 1947–1964. An attempt was made to at least list all of the references in this area; however, in some cases, such as the use of complex aluminohydrides as polymerization catalysts, this could not be done. This problem was caused by the large number of patents in the area;

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most contributed little to the understanding of the chemistry and some could hardly be distinguished one from the other as to the contribution that was made. Discussion in some detail has been attempted of what the author considers to be the most significant and meaningful contributions; for example, the significance of recent work by H. C. Brown on metal alkoxyaluminohydrides ($MAlOR_nH_{4-n}$) to the mechanism of $MAlH_4$ reduction of ketones. The bonding implications in the new "triple metal hydrides" reported by Wiberg are discussed in some detail.

It is hard not to come to the conclusion that the area of complex metal hydride chemistry is "wide open" to the inorganic chemist with many obvious starting points that could lead to significant contributions. The conclusion has also been reached that there are fundamental contributions in this area that are taken for granted but should be checked because of lack of experimental data or, in some cases, poor judgment in arriving at conclusions. Some of these areas are pointed out in the ensuing discussion. If the reader does not agree with some of the criticisms leveled by the author, then he may be stimulated to prove his point by experimentation. If many assumptions of fundamental significance in this area can be substantiated by more experimentation, future progress will be more rapid.

Needless to say, all work concerned with complex metal hydride chemistry must be carried out in air and moisture-free systems. Commercially available nitrogen dry-boxes have improved considerably in the last 10 years and are invaluable for carrying out experimental work in this area. In addition to these precautions one should be aware of the safety problems in working with complex metal hydrides. Complex metal hydrides are powerful reducing agents and contain a relatively large amount of immediately releasable hydrogen. A number of serious explosions have been reported involving lithium and sodium aluminum hydride in tetrahydrofuran and dimethyl ether solvent (*11*, *77*, *90*).

## II. Historical

The father of metal hydride chemistry could be considered to be the German chemist Alfred Stock, who between 1912 and 1932 published over seventy papers dealing with the boron and silicon hydrides. The contributions of Stock and his students represented most of what was known about hydride chemistry up to 1930. The next major surge in metal hydride chemistry was made by H. I. Schlesinger, H. C. Brown, and A. E. Finholt at the University of Chicago between 1930 and 1950. It was in this group that the first complex metal hydrides, $Al(BH_4)_3$ and $Be(BH_4)_2$, were prepared in 1939. This group became actively engaged in the preparation of new complex metal hydrides as part of a classified program during World War II. It was during this effort that most of the known stable complex boro- and aluminohydrides were prepared. It is interesting that, although sodium borohydride was prepared several years prior to lithium aluminum hydride, the latter compound was reported first and hence received the most notoriety and research effort in exploring its utility. The next surge in hydride chemistry came in the early 1950's and, as in the earlier surges, appears to have slackened considerably after several years' effort by the major contributors. In this last era have been the most exciting developments to date. On the one hand, Egon Wiberg at Munich, a student of Stock, has contributed greatly in the area of new complex metal hydride preparations. On the other hand, H. C. Brown of Purdue University, a student of Schlesinger, has contributed mostly to the inorganic chemistry and applications of complex metal hydrides to organic synthesis. It is mainly the contributions of these workers that account for the present state of development of the area of complex aluminohydrides.

## III. Lithium Aluminum Hydride

By far the most widely explored complex aluminohydride is lithium aluminum hydride. It has been until recently the only commercially available complex aluminohydride. For this reason more information is available on this aluminohydride than any other.

### A. PROPERTIES AND STRUCTURE

Lithium aluminum hydride (hereafter referred to as $LiAlH_4$) is a white crystalline solid stable in dry air at room temperature, but very susceptible to moisture and protic solvents. As purchased from its sole distributor (Metal Hydrides, Inc.) it is a hard, lumpy, gray solid, which can be purified by recrystallization from an ether-benzene solution. Most often $LiAlH_4$ is used as a standardized ether solution prepared by solution of the commercial grade solid in anhydrous diethyl ether followed by filtration of the insoluble gray residue.

One of the advantages of $LiAlH_4$ as a reducing agent over other complex metal hydrides lies in its greater solubility in ether-type solvents, especially diethyl ether. The solubility of $LiAlH_4$ in some typical ether solvents is shown in Table I. $LiAlH_4$ in general is stable in these solvents at room temperature for extended periods of time (several months). When $LiAlH_4$ is employed in ether solution at elevated temperatures some cleavage of the ether solvent as well as thermal decomposition of the $LiAlH_4$ is experienced.

Finholt and Jacobson (*39*) have reported that solid $LiAlH_4$ will decompose at room temperature slowly over a period of several months. The evidence is based on the gradual graying of the white crystalline solid with time, indicating aluminum deposition. The decomposition rate can be

TABLE I
SOLUBILITY OF $LiAlH_4$ IN ETHER SOLVENTS

| Solvent | Solubility (gm/100 gm solvent) |
|---|---|
| Diethyl ether | 29 |
| Tetrahydrofuran | 13 |
| Dimethylcellosolve (diglyme) | 10 |
| Dibutyl ether | 2 |
| Dioxane | 0.1 |

accelerated or decreased, depending on the presence of impurities. For example, the decomposition of $LiAlH_4$ in the solid state or in solution can be increased by the addition of finely divided metals such as titanium, silicon, iron, copper, aluminum, boron, mercury, or silver (*148*). Wiberg and Lacal (*126*) have used the decomposition of $LiAlH_4$ by these metals to explain the darkening sometimes observed in the preparation of $LiAlH_4$ by the method of Finholt. On the other hand, it has been claimed by Bragdon (*17*) that solid $LiAlH_4$ or ether solutions of $LiAlH_4$ can be stabilized by the addition of small amounts of 1,4-dioxane, lower alkyl cellosolves, or tertiary amines. Wiberg and Lacal also reported increased stabilization of ether solutions of $LiAlH_4$ by the addition of a small amount of lithium hydride.

The thermal decomposition of $LiAlH_4$ at elevated temperatures has been studied by several workers. Garner and Haycock (*47*) found that $LiAlH_4$ decomposed on heating (100°C), exhibiting three distinct stages of decomposition. These stages were reflected in an S-shaped curve when decomposition (measured as a function of hydrogen evolution) was plotted vs. time. The different stages involved (1) an initial reaction on the surfaces of the grains of the hydride, which was at first rapid and then slowed down to a constant rate, (2) an accelerated reaction passing through a maximum and becoming very slow after 2 hydrogen atoms per molecule of $LiAlH_4$ had been liberated, and finally (3) a slow reaction, during which a third hydrogen atom was liberated. Equations used to depict these steps are as follows:

$$LiAlH_4 \rightarrow LiAlH_2 + H_2 \qquad (1)$$

$$LiAlH_2 \rightarrow LiH + H_2 \qquad (2)$$

This interpretation is similar to that suggested earlier by Finholt *et al.* (*41*) for the decomposition of $LiBH_4$. The following steps were suggested:

$$LiBH_4 \rightarrow LiBH_2 + H_2 \qquad (3)$$

$$LiBH_2 \rightarrow LiH + B + H_2 \qquad (4)$$

Mikheeva and co-workers (*75*) have studied the thermal decomposition of $LiAlH_4$ under vacuum and found greater stability than was observed at atmospheric pressure. At 154°–161°, 50% of the available hydrogen was lost, at 197°–227° another atom of hydrogen was lost, and at 580°–586° the final hydrogen was lost. The residue consisted of a high purity lithium-aluminum alloy. The interpretation of these results was essentially the same as proposed by Garner and Haycock, the last hydrogen being lost via thermal decomposition of LiH to Li + $H_2$.

The interpretation of the decomposition of $LiAlH_4$ as proceeding through the intermediate $LiAlH_2$ seems logical on the basis that exactly 50%, and no more, of the total hydrogen in $LiAlH_4$ is liberated when this compound is heated to 100°. Unfortunately no one has isolated and identified the proposed decomposition products ($LiAlH_2$ or $LiBH_2$) in order to establish without doubt the decomposition scheme and the existence of these compounds. Thus it is possible that the decomposition behavior can be explained in another way. On the basis of a recent report by Zakharkin and Gavrilenko (*153*) concerning the reaction of NaH and $NaAlH_4$ to produce $Na_3AlH_6$, one should consider the possibility that thermal decomposition of $LiAlH_4$ proceeds through $Li_3AlH_6$ as an intermediate according to the following sequence of reactions:

$$2LiAlH_4 \rightarrow 2LiH + Al + 3H_2 \quad (5)$$

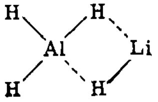
$$2LiH + LiAlH_4 \rightarrow Li_3AlH_6 \quad (6)$$

$$3LiAlH_4 \rightarrow Li_3AlH_6 + 2Al + 3H_2 \quad (7)$$

Thus, the above sequence of reactions is also consistent with the decomposition data, namely, exactly 50% loss of $H_2$ at 100°. It would appear that the decomposition products will need to be isolated and identified before one can distinguish between the two possibilities.

Lippincott (*68*) recorded the infrared and Raman spectra for a 1.28 *M* solution of $LiAlH_4$ in diethyl ether. The spectra were interpreted as being consistent with a tetrahedral model for the $(AlH_4)^-$ ion in solution. $LiAlH_4$ in ether solution exhibits two intense bands with peaks at 764 and 1740 $cm^{-1}$. The broadness of the Al—H band as compared to that of other Al—H compounds (e.g. $HAlCl_2$, $H_2AlCl$) was attributed to the partial splitting of triply degenerate modes of vibration by liquid forces. Nuclear magnetic resonance studies have shed little light on the structure of $LiAlH_4$.

Further information concerning the structure of $LiAlH_4$ was presented by Paddock (*84a*) and Wiberg and Schrauzer (*144*), based on conductivity data of $LiAlH_4$ in diethyl ether solution. Paddock reported a specific conductance of $4.43 \times 10^{-5}$ $ohm^{-1}$ $cm^{-1}$ for a 1.0 *M* solution at 15°, whereas Wiberg reported a value of $6.6 \times 10^{-5}$ $ohm^{-1}$ $cm^{-1}$ for a 0.7 *M* solution at 20°. A significant comparison of these conductivity data can be made with that of a 0.7 *M* solution of $LiBH_4$ in diethyl ether. The value reported by Wiberg is $3 \times 10^{-6}$ $ohm^{-1}$ $cm^{-1}$ at 20°. Thus it would appear that, in diethyl ether solution, $LiAlH_4$ is more dissociated than $LiBH_4$. That Harris and Meibohm (*55*) have determined by X-ray diffraction the structure of $LiBH_4$ to consist of lithium ions and borohydrides ions strengthens the representation of $LiAlH_4$ in diethyl ether solution as consisting of lithium ions and aluminohydride ions. Such a representation does not appear consistent with the structure proposed by Wiberg. However, in a solvent



(I)

of low dielectric constant such as diethyl ether, ion pairs and structures such as (I), proposed by Wiberg, should be considered. Wiberg also reported conductances for $LiAlH_4$ and $LiBH_4$ in tetrahydrofuran to be 100 times greater than in diethyl ether. This is not too surprising since the dielectric constant at 20° for diethyl ether is 4.35 and for tetrahydrofuran 7.84.

Molecular association studies (ebullioscopic) of $LiAlH_4$ in diethyl ether were reported by Wiberg and Graf (*123*). They found that the molecular weight of $LiAlH_4$ increased with an increase in concentration. In 0.08 *M* solution the apparent molecular weight was twice that of the calculated value, and in 0.8 *M* solution 3 times the calculated value. These results were interpreted in terms of associated species linked by hydrogen bridge bonds.

## B. Preparations

The preparation of $LiAlH_4$ was first reported by Finholt *et al.* in 1947 (*41*, *92*). The method involved the reaction of lithium hydride and aluminum chloride in diethyl ether solution and produced $LiAlH_4$ in 86% yield. The reaction was carried out by addition of an ether solution of aluminum chloride to a refluxing slurry of lithium hydride (used in excess) in diethyl ether. Lithium chloride precipitated from the reaction mixture and was filtered from the solution of $LiAlH_4$ along with the excess lithium hydride:

$$4LiH + AlCl_3 \rightarrow LiAlH_4 + LiCl \qquad (8)$$

The white crystalline $LiAlH_4$ was then isolated by precipitation from the ether solution on addition of benzene. Two important considerations for the success of this reaction were found to be the particle size of the lithium hydride and the presence of a small amount of $LiAlH_4$ initiator. Using 20–60-mesh lithium hydride, only an insignificant amount of reaction took place after 2 weeks in refluxing ether. In all probability precipitated lithium chloride coated the relatively large particles of lithium hydride. Grinding the lithium hydride to a fine powder before use reduced reaction times to a matter of several hours. The induction period normally experienced in the reaction led to complications in that once the reaction started it proceeded with almost uncontrollable speed. In the presence of a small initial quantity of $LiAlH_4$, the reaction begins at once at a rate which can be controlled by the rate of addition of the aluminum chloride solution.

All of the $LiAlH_4$ produced today on a commercial scale is made by the reaction of lithium hydride and aluminum chloride in diethyl ether (hereafter referred to as the Schleslinger process). The importance of this process commercially is exemplified by the many articles and patents reporting improvements of the process. For example, Wiberg has reported two improvements in the Schleslinger process. One improvement describes the stabilization of solutions of $LiAlH_4$ made by the Schlesinger process by addition of lithium hydride (*115*) and the other describes initiation of the reaction by the addition of iodine (*114*). More significantly, Wiberg and Schmidt claim (*140*) an improved method for preparing $LiAlH_4$ by substitution of $AlBr_3$ for $AlCl_3$:

$$4LiH + AlBr_3 \rightarrow LiAlH_4 + 3LiBr \qquad (9)$$

The use of $AlBr_3$, according to Wiberg and Schmidt, eliminates the necessity of pulverizing the lithium hydride, using it in excess, and adding $LiAlH_4$ as an initiator. On the other hand, lithium bromide has appreciable solubility in diethyl ether, thereby contaminating $LiAlH_4$ made by this process modification. Fortunately, the presence of lithium bromide appears to be beneficial, if anything, when $LiAlH_4$ made from aluminum bromide is used as a reducing agent.

Significant activity in attempting to improve the Schlesinger reaction is further indicated by the number of patents issued to various chemical companies. Hans-Heinrich-Hütte (*Mettallgesellschaft*), for example, has been issued process improvement patents which claim significant improvements when $AlBr_3$ is substituted for $AlCl_3$ (*53*, *141*, *143*). Other reports from the same source describe purification of the resulting $LiAlH_4$ from LiBr (*142*). Further improvements described by others involve elimination of the induction period, when aluminum chloride is used, by using diethyl ether dried and distilled over $LiAlH_4$ (*76*). Exploration of optimum conditions relating to reaction temperature, rate of addition of aluminum chloride, etc., have been reported by Mikheeva and co-workers (*73*, *74*). Improvements in the Schlesinger reaction involving use of a mixture of aluminum bromide and aluminum chloride (1:3 to 1:30 ratio) have been reported by Schultz and Schnekenberger (*94*, *95*) and Semenenko and co-workers (*98*). Several other patents concerning the Schlesinger process exist; however, they do not appear to add anything new to what has been reported.

The major drawback to the use of $LiAlH_4$ as a reducing agent for both organic and inorganic reductions has been the high cost of this compound produced by the Schlesinger route. More recently Ashby and co-workers have reported (*2*, *3*, *7*) a direct route to $LiAlH_4$ as well as other alkali metal complex hydrides. This new route, when in commercial operation, should reduce the cost of these reagents considerably, and thereby increase their usage. The process described involves the reaction of an alkali metal or its hydride with aluminum and hydrogen at elevated temperature and pressure in either hydrocarbon or ether solvent. At 140° and 5000 psi hydrogen, reaction in tetrahydrofuran was complete in 5 hours producing $LiAlH_4$ in 96% yield:

$$LiH + Al + H_2 \rightarrow LiAlH_4 \tag{10}$$

In contrast to the Schlesinger reaction, the direct synthesis uses only 1 mole of lithium hydride per mole of product instead of 4 moles, the source of aluminum is aluminum metal rather than aluminum chloride, and the diluent can be a hydrocarbon rather than ether. Triethylaluminum used as a catalyst was found to both reduce the induction period of the reaction and increase the yield. The effects of temperature, pressure, solvent, catalyst, and source of aluminum were studied.

Since lithium metal melts at about 180° (considerably above the decomposition temperature of $LiAlH_4$), it is desirable to use lithium hydride in the reaction rather than lithium metal. However, sodium melts at 95° and therefore for the preparation of $NaAlH_4$ (decomposes at 185°) it is advantageous to begin with sodium metal, which is rapidly hydrogenated to sodium hydride *in situ* under the reaction conditions. For this reason and because sodium metal is much less expensive than lithium metal (16 cents vs. $9.00/lb), it is more economical to produce $NaAlH_4$ by the direct synthesis. $NaAlH_4$ can then be used to produce $LiAlH_4$ by the method reported by Nöth (*80*), Ashby, Robinson and co-workers (*7*, *31*), and Clasen (*21*). This method involves the metathetical reaction of $NaAlH_4$ and lithium chloride in diethyl ether at room temperature:

$$NaAlH_4 + LiCl \rightarrow LiAlH_4 + NaCl \tag{11}$$

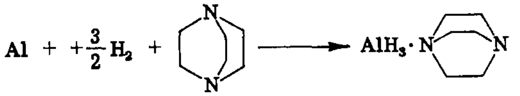
Although $NaAlH_4$ and lithium chloride are insoluble in diethyl ether, the reaction proceeded smoothly and rapidly at room temperature when a small amount of $LiAlH_4$ was used as an initiator. When the reaction was complete, the insoluble sodium chloride was filtered and the $LiAlH_4$ easily isolated from the ether solution by benzene addition followed by the removal of diethyl ether under vacuum. The favorable economics of producing $LiAlH_4$ by the metathetical exchange reaction is based on the lower cost of LiCl per pound of contained lithium as compared to lithium metal.

Sometime after the initial report by Ashby (*2*) describing the direct route to the complex metal hydrides, Clasen (*21*) reported similar results; however, reaction conditions and yields were not as attractive as described in the earlier report. Reaction conditions necessitated the ball milling of both sodium hydride and aluminum powder to produce 18% yield of $NaAlH_4$. No yield data were given for the preparation of $LiAlH_4$. Sometime later Hoffman and Spurlin (*58*) reported conditions for carrying out the direct synthesis of alkali metal aluminohydrides; however, the maximum yield reported for $LiAlH_4$ was 2.6% and, for $NaAlH_4$, 67%. A process improvement involving the use of amine-boranes as initiators was reported by Powers (*85*), and the use of lithium-aluminum alloy (*59*) in place of lithium and aluminum metal has been reported to produce $LiAlH_4$ in 80% yield.

Ruff and Hawthorne (*89*) reported what appears to be a convenient laboratory route to $LiAlH_4$ as well as other complex metal hydrides. The method involves the reaction of an amine-alane with the appropriate alkali metal or alkaline earth hydride. $LiAlH_4$ was prepared by reaction of lithium hydride (excess) and trimethylamine-alane in diethyl ether solvent:

$$LiH + AlH_3{\cdot}N(CH_3)_3 \rightarrow LiAlH_4 + N(CH_3)_3 \qquad (12)$$

The reaction mixture was refluxed for 2 hours followed by filtration of unreacted lithium hydride. Benzene extraction of the unreacted amine-alane after ether removal resulted in the isolation of $LiAlH_4$ in about 20% conversion. No attempt was made to optimize the yield by pulverizing the lithium hydride prior to use. Although the conversion was low it would appear that the yields are high and that higher conversions could be accomplished with some effort. This method appears to be of some significance for two reasons; first, the alkali and alkaline earth hydrides are commercially available and, second, the direct synthesis of an amine-alane has been reported by Ashby (*4*), suggesting the possibility that amine-alanes may also be commercially available soon. Triethylenediamine-alane was produced by the reaction below in 96% yield:



(13)

Finally, Finholt (*38*) has described a two-step process for preparing $LiAlH_4$ which reduces the number of moles of lithium hydride required to produce 1 mole of $LiAlH_4$ from 4 to 1:

$$3NaAlH_4 + AlX_3 \rightarrow 4AlH_3 + 3NaX \quad (14)$$

$$4AlH_3 + 4LiH \rightarrow 4LiAlH_4 \quad (15)$$

$$3NaAlH_4 + AlX_3 + 4LiH \rightarrow 4LiAlH_4 + 3NaX \quad (16)$$

The $NaAlH_4$ used in this process is also obtained by a two-step process. The equations below indicate that 4 moles of $NaAlH_4$ are produced from 3 moles:

$$3NaAlH_4 + AlX_3 \rightarrow 4AlH_3 + 3NaX \quad (17)$$

$$4AlH_3 + 4NaH \rightarrow 4NaAlH_4 \quad (18)$$

$$3NaAlH_4 + AlX_3 + 4NaH \rightarrow 4NaAlH_4 + 3NaX \quad (19)$$

Yields are high, allowing 3 moles of $NaAlH_4$ to be recycled, thus resulting in a net production of $NaAlH_4$. The $NaAlH_4$ produced according to Eqs. (17–19) is then available to produce $LiAlH_4$ according to Eqs. (14–16).

## C. REACTIONS

### 1. *Protic Compounds*

*a. Water.* $LiAlH_4$ added to water reacts with explosive violence generating hydrogen. The reaction can be moderated by dissolving the required amount of water in an organic diluent such as tetrahydrofuran or dioxane before addition. According to Finholt *et al.* (*41, 92*), the equation describing the reaction can be written as either Eq. (20) or Eq. (21):

$$LiAlH_4 + 4H_2O \rightarrow LiOH + Al(OH)_3 + 4H_2 \quad (20)$$

$$LiAlH_4 + 2H_2O \rightarrow LiAlO_2 + 4H_2 \quad (21)$$

The evolution of hydrogen from $LiAlH_4$ is quantitative. Standard solutions of $LiAlH_4$ in diglyme have been used to determine within ±0.005% the water content of organic liquids, especially hydrocarbons (*8, 113*). Hydrogen evolution as a method of determining $LiAlH_4$ purity has been described by several workers (*41, 71, 87, 126*).

$LiAlH_4$ has been found to react with $D_2O$ at 0° to produce DH in 99% purity (*113*):

$$LiAlH_4 + 4D_2O \rightarrow LiOD + Al(OD)_3 + 4DH \quad (22)$$

Small amounts of $H_2$ and $D_2$ were also produced which could be attributed to some small amount of decomposition during hydrolysis and Al metal impurity, respectively. Reaction of $LiAlH_4$ with water containing tritium has been used to determine tritium activity in samples of cholesterol-$H^3$ (*16*).

*b. Ammonia, Phosphine, and Arsine.* Finholt and co-workers (*44*) reported that solutions of $LiAlH_4$ in diethyl ether or tetrahydrofuran react vigorously with ammonia to liberate hydrogen. From $H_2$ evolution data the following reaction was postulated:

$$2LiAlH_4 + 5NH_3 \rightarrow [LiAlH(NH_2)_2]_2NH + 6H_2 \quad (23)$$

The same workers also reported the reaction of 1° and 2° amines with $LiAlH_4$. Although details were not given, the reactions were proposed to have taken place according to the following equations:

$$LiAlH_4 + 4RNH_2 \rightarrow LiAl(NRH)_4 + 4H_2 \qquad (24)$$

$$LiAlH_4 + 4R_2NH \rightarrow LiAl(NR_2)_4 + 4H_2 \qquad (25)$$

The first hydrogen of the 1° amine reacts rapidly, but the second hydrogen reacts much more slowly (*67*).

Finholt and co-workers (*44*) reported a more detailed study concerning the reaction of $LiAlH_4$ not only with ammonia, but also with phosphine and arsine. Under the proper conditions both $LiAlH_4$ and $NaAlH_4$ reacted according to Eq. (26):

$$MAlH_4 + 4EH_3 \rightarrow MAl(EH_2)_4 + 4H_2 \qquad (26)$$

where M = Li, Na; and E = N, P, As. Hydrolysis of $MAl(EH_2)_4$ released the group V hydrides quantitatively according to Eq. (27):

$$MAl(EH_2)_4 + 4H_2O \rightarrow 4EH_3 + MAl(OH)_4 \qquad (27)$$

Equation (26) was realized when ammonia was reacted in the absence of a solvent or in the presence of diethyl ether or diglyme, provided the ammonia-to-hydride ratio was high. When the hydride-to-ammonia ratio was high, all three ammonia hydrides were replaced.

In diglyme and tetrahydrofuran, phosphine reacted with $LiAlH_4$ according to Eq. (26) to form a soluble product. The reaction with ammonia formed insoluble products. The solubility factor allowed nucleophilic substitution reactions to be carried out with $LiAl(PH_2)_4$ and several organic compounds. In diglyme and tetrahydrofuran there was no tendency to form products other than according to Eq. (26), even at high hydride-to-phosphine ratios. However, in diethyl ether almost 3 moles of hydrogen per mole of phosphine were evolved. The rate of reaction of the group V hydrides with $LiAlH_4$ was $NH_3 > AsH_3 > PH_3$. This order is in keeping with relative electronegativities and base strengths.

*c. Alcohols.* The reaction of alcohols with $LiAlH_4$ has recently been studied in detail by Brown and Shoaf (*18*). Methyl, ethyl, isopropyl, *sec*-butyl, and *t*-butyl alcohols were studied and the solvents employed were diethyl ether, tetrahydrofuran, and diglyme. In general the reactions proceeded by the following series of steps (although several exceptions were noted):

$$LiAlH_4 + ROH \rightarrow LiAlH_3OR + H_2 \qquad (28)$$

$$LiAlH_3OR + ROH \rightarrow LiAlH_2(OR)_2 + H_2 \qquad (29)$$

$$LiAlH_2(OR)_2 + ROH \rightarrow LiAlH(OR)_3 + H_2 \qquad (30)$$

$$LiAlH(OR)_3 + ROH \rightarrow LiAl(OR)_4 + H_2 \qquad (31)$$

When methyl alcohol was added to $LiAlH_4$ in tetrahydrofuran or diglyme, it was shown that stepwise reaction took place producing soluble $LiAlH_n(OCH_3)_{4-n}$ compounds according to the ratio of the reactants. For example, $LiAl(OCH_3)_3H$ was readily prepared by reaction of 3 moles of methyl alcohol with 1 mole of $LiAlH_4$ in tetrahydrofuran. In diethyl ether solution the di- and trisubstituted products were insoluble, complicating the identification of the products as pure compounds or mixtures. The reaction of $LiAlH_4$ with ethyl alcohol was more complicated. Precipitation of solids during the addition of the second and third moles of alcohol, in all the solvents studied, prevented the isolation of pure products. Both isopropyl and *sec*-butyl alcohols reacted with $LiAlH_4$ to yield complex mixtures involving the formation and precipitation of major amounts of the tetraalkoxy derivative. The reaction of $LiAlH_4$ with *t*-butyl alcohol can be controlled to yield lithium di- and tri-*t*-butoxyaluminohydride without difficulty. The fourth hydrogen atom is removed slowly by reaction of the trisubstituted product and *t*-butyl alcohol in tetrahydrofuran or diglyme at 60°–80°. The lithium alkoxyaluminohydrides prepared by this method are shown in Table II.

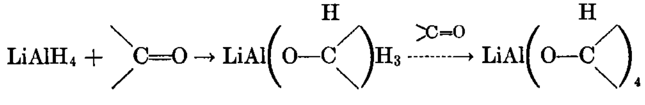
TABLE II
PREPARATION[a] OF LITHIUM ALKOXYALUMINOHYDRIDES BY THE REACTION:
$LiAlH_4 + n\mathrm{ROH} \rightarrow LiAl(OR)_nH_{4-n} + nH_2$

| Compound | R = Me | R = Et | R = *i*-Pr | R = *t*-Bu |
|---|---|---|---|---|
| $LiAl(OR)_4$ | 1, 2, 3 | 1, 2, 3 | 1, 2, 3 | 1, 2 |
| $LiAl(OR)_3H$ | 1, 2, 3 | — | — | 1, 2, 3 |
| $LiAl(OR)_2H_2$ | 1, 2, 3 | 1, 2 | — | 1, 2, 3 |
| $LiAl(OR)H_3$ | 2, 3 | 1, 2, 3 | 2 | 1, 2, 3 |

[a] 1—Diethyl ether solvent; 2—tetrahydrofuran solvent; 3—diglyme solvent.

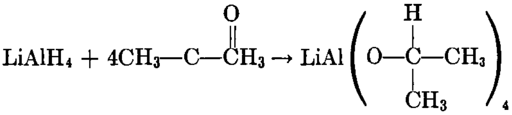
The redistribution of $LiAlH_4$-$LiAl(OR)_4$ mixtures was also studied by Brown and Shoaf (*18*). Although $LiAl(OCH_3)_3H$ was readily prepared by the redistribution of $LiAlH_4$ and $LiAl(OCH_3)_4$ in tetrahydrofuran, redistributions involving other alkoxy compounds were slow and mixtures of products were formed. When $LiAlH_4$ and LiAl(O-*t*-Bu)$_4$ were refluxed in diethyl ether for 1 hour, no redistribution was observed.

These results appear to be helpful in attempting to understand the mechanism of $LiAlH_4$ reduction of organic functional compounds, such as ketones. The steps proposed for this reduction process are as follows:



$$\mathrm{LiAlH_4} + \rangle\mathrm{C{=}O} \rightarrow \mathrm{LiAl}\left(\mathrm{O{-}}\overset{\mathrm{H}}{\mathrm{C}}\langle\right)\mathrm{H_3} \xrightarrow{\rangle\mathrm{C{=}O}} \mathrm{LiAl}\left(\mathrm{O{-}}\overset{\mathrm{H}}{\mathrm{C}}\langle\right)_4 \qquad (32)$$

It is significant to the understanding of this reaction mechanism whether a stepwise reduction takes place producing an intermediate lithium alkoxyaluminohydride which then attacks another molecule of ketone, or whether disproportionation of the intermediate lithium alkoxyaluminohydride takes place such that $LiAlH_4$ is always the attacking species. The steric requirement and electronic environment are quite different for the two possibilities. The reaction of $LiAlH_4$ with acetone (the simplest ketone possible) produces lithium tetra-*i*-propoxyaluminohydride:



$$LiAlH_4 + 4CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3 \rightarrow LiAl\left(O{-}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}{-}CH_3\right)_4 \qquad (33)$$

Brown found that precipitation of $LiAl(O\text{-}i\text{-}Pr)_4$ is rapid when 1, 2, or 3 moles of isoproponol is added to $LiAlH_4$, and that redistribution is poor when $LiAlH_4$ and $LiAl(O\text{-}i\text{-}Pr)_4$ are refluxed in diethyl ether. Since $LiAlH_4$ is more reactive toward ketones than $LiAl(OR)_nH_{4-n}$ compounds, the attacking species will depend on the rate of disproportionation of the intermediate $LiAl(OR)_nH_{4-n}$ compound. Those $LiAl(OR)_nH_{4-n}$ compounds that disproportionate rapidly to $LiAlH_4$ and $LiAlOR_4$ will exhibit $LiAlH_4$ as the attacking species. Those $LiAl(OR)_nH_{4-n}$ compounds that do not disproportionate rapidly will result in stepwise reduction in which the attacking species increases in steric requirement as the reaction proceeds. These conclusions are consistent with the results reported by Haubenstock and Eliel (*53a*) concerning the reduction of 3,3,5-trimethylcyclohexone with lithium alkoxyaluminohydrides.

*d. Acids.* As would be expected, $LiAlH_4$ reacts violently with protic acids. For example, $LiAlH_4$ reacts with hydrocyanic (*149*) and hydrazoic (*117*) acids in diethyl ether solution at −80° to liberate the theoretical amount of hydrogen.

$$LiAlH_4 + 4HCN \rightarrow LiAl(CN)_4 + 4H_2 \qquad (34)$$

$$LiAlH_4 + 4HN_3 \rightarrow LiAl(N_3)_4 + 4H_2 \qquad (35)$$

The product from hydrazoic acid is stable at room temperature in the absence of air or moisture, but is explosive to shock. The product from hydrocyanic acid is not stable at room temperature.

### *2. Metal and Metalloid Halides*

Finholt and co-workers (*41*) in 1947 reported several reactions of metal and metalloid halides with $LiAlH_4$ to form metal aluminum hydrides. Since that time, almost every metal or metalloid halide available has been reacted with $LiAlH_4$. If the metal aluminum hydride formed by this reaction, Eq.

(36), is not stable, then a mixture of the metal hydride and aluminum hydride is isolated according to Eq. (37):

$$MX_n + nLiAlH_4 \rightarrow M(AlH_4)_n + nLiX \quad (36)$$

$$M(AlH_4)_n \rightarrow MH_n + nAlH_3 \quad (37)$$

*a. Group IB: Cu, Ag, Au.* The reaction of copper halides and $LiAlH_4$ has been studied by Warf and Feitknecht (*109*) and Wiberg and Henle (*125*). The former workers found that reaction of $LiAlH_4$ and cupric chloride in diethyl ether produced metallic copper and lithium chloride, whereas reaction with cuprous iodide gave a product having a H:Cu ratio of 0.5. The latter workers found that reaction of $LiAlH_4$ and cuprous iodide in pyridine solvent produced a solution of cuprous hydride:

$$LiAlH_4 + 4CuI \rightarrow 4CuH + LiI + AlI_3 \quad (38)$$

In this reaction the aluminum iodide precipitated and the cuprous hydride remained in solution. The hydride product precipitated after $AlI_3$ filtration by addition of diethyl ether to the pyridine solution. The product was a reddish brown solid reported to be stable to 60°:

$$CuH \xrightarrow{60^\circ} Cu + H_2 \quad (39)$$

The cuprous hydride reported here cannot be, by virtue of its solubility in pyridine and stability to water, an ionic hydride similar to the Group IA metal hydrides; however, it must be a chemical compound rather than a solution of hydrogen in copper.

Wiberg and Henle (*125*) also reported the preparation of silver aluminum hydride by reaction of $LiAlH_4$ and silver perchlorate in diethyl ether at −80°:

$$AgClO_4 + LiAlH_4 \rightarrow AgAlH_4 + LiClO_4 \quad (40)$$

Evidence of reaction at this low temperature is based on the precipitation of silver aluminum hydride from the reaction mixture as a gold-colored solid. However, the product decomposed on warming to −50°, producing silver, aluminum, and hydrogen:

$$AgAlH_4 \rightarrow AgH + AlH_3 \rightarrow Ag + Al + 2H_2 \quad (41)$$

The decomposition of aluminum hydride was proposed to be accelerated by the presence of finely divided silver. The reaction of $AgClO_4$ and $LiAlH_4$ would appear to be extremely dangerous. This combination of oxidizing and reducing agent seems to have all of the necessary chemical make-up for a high energy rocket propellant.

Wiberg (*116*) has proposed that little hope exists for the preparations of $AuAlH_4$ or even AuH by reaction of $LiAlH_4$ and gold salts or by any other reaction. He based this conclusion on the extrapolated value for the decomposition temperature of AuH which was −155°.

*b. Group IIA: Be, Mg.* Wiberg and Bauer (*119*) reported the preparation of beryllium aluminum hydride by reaction of $LiAlH_4$ and beryllium chloride in ether solution at room temperature:

$$2LiAlH_4 + BeCl_2 \rightarrow Be(AlH_4)_2 + 2LiCl \tag{42}$$

The product was soluble in the reaction mixture and was isolated as a white crystalline solid by removal of the solvent under vacuum after filtration of the insoluble lithium chloride. The product was reported to be water-sensitive; however, no thermal stability data were given. (For further discussion of this reaction, see Section VII.)

The reaction of $LiAlH_4$ and magnesium bromide in diethyl ether was reported by Wiberg and Bauer (*118*) to produce magnesiumaluminum hydride in high yield:

$$2LiAlH_4 + MgBr_2 \rightarrow Mg(AlH_4)_2 + 2LiBr \tag{43}$$

The product was reported to be soluble in ether and therefore difficult to separate from the lithium bromide by-product which is also soluble. The product was reported to be stable at 140°. (For further discussion of this reaction, see Section VIII.)

The same workers also reported the reduction of Grignard compounds using $LiAlH_4$ in diethyl ether (*118*):

$$RMgX + LiAlH_4 \rightarrow RMgAlH_4 + LiX \tag{44}$$

This is an interesting reaction worthy of more investigation because of its implications to the composition of Grignard compounds in diethyl ether solution.

*c. Group IIB: Zn, Cd, Hg.* Wiberg and co-workers (*147*) reported that the reaction of $LiAlH_4$ and zinc iodide in diethyl ether at −40° produced zinc hydride:

$$2LiAlH_4 + ZnI_2 \rightarrow ZnH_2 + 2AlH_3 + 2LiI \tag{45}$$

The reaction was surmised to proceed through the intermediate formation of $Zn(AlH_4)_2$; however, this product was not detected. The zinc hydride produced in the reaction was reported to be a white solid, insoluble in diethyl ether and stable to 90°. Somewhat more stable than zinc hydride is its iodine derivative, which is stable to 110°:

$$ZnI_2 + LiH \rightarrow HZnI + LiI \tag{46}$$

$$2HZnI \rightarrow Zn + H_2 + ZnI_2 \tag{47}$$

Wiberg and Henle (*124*) reported that the reaction of $LiAlH_4$ and cadmium iodide at −70° in tetrahydrofuran produced cadmium hydride:

$$2LiAlH_4 + CdI_2 \rightarrow CdH_2 + 2AlH_3 + 2LiI \tag{48}$$

Although the reaction was presumed to proceed through the formation of $Cd(AlH_4)_2$, this compound was not detected. The cadmium hydride was insoluble in the reaction medium in which it was prepared. Aluminum hydride apparently did not polymerize at such a low temperature and therefore remained in solution. The cadmium hydride decomposed at −20° to cadmium and hydrogen.

Wiberg and Henle (*124*) also reported the reaction of $LiAlH_4$ and mercury iodide in diethyl ether-tetrahydrofuran-petroleum ether solvent mixture at −135° to produce mercury hydride:

$$2LiAlH_4 + HgI_2 \rightarrow HgH_2 + 2AlH_3 + 2LiI \tag{49}$$

The white solid mercury hydride was reported to decompose at −125° to mercury and hydrogen.

*d. Group IIIA: B, Al, In, Ga, Te.* The reaction of $LiAlH_4$ and boron trifluoride (*72*), boron trichloride (*41*), and boron tribromide (*109*) at room temperature in diethyl ether is reported to produce diborane in high yield:

$$3LiAlH_4 + BX_3 \rightarrow 2B_2H_6 + 3AlX_3 + 3LiX \tag{50}$$

The mode of addition in this reaction appears to be important. For example, if the boron halide is added to $LiAlH_4$, no diborane is released from the reaction mixture until about three fourths of the halide has been added. On the other hand, if $LiAlH_4$ is added to the boron halide, a smooth evolution of diborane begins at once. The reason diborane is liberated belatedly in the former case can be explained on the basis of reaction of diborane with $LiAlH_4$ and the liberated by-product, $LiBH_4$:

$$LiAlH_4 + 2B_2H_6 \rightarrow LiBH_4 + Al(BH_4)_3 \tag{51}$$

$$LiBH_4 + \tfrac{1}{2}B_2H_6 \rightarrow LiB_2H_7 \tag{52}$$

Both reactions, Eqs. (51) and (52), are fast and have been previously reported (*19, 41*). Diborane can be liberated from these intermediates according to the following known reactions involving the addition of boron halide:

$$6LiB_2H_7 + 2BX_3 \rightarrow 7B_2H_6 + 6LiX \tag{53}$$

$$3LiBH_4 + BX_3 \rightarrow 2B_2H_6 + 3LiX \tag{54}$$

$$Al(BH_4)_3 + BX_3 \rightarrow AlX_3 + 2B_2H_6 \tag{55}$$

These reactions also are consistent with the immediate liberation of diborane from the reaction of $LiAlH_4$ and boron halide when $LiAlH_4$ is added to the boron halide.

The reaction of $LiAlH_4$ and boron trihalide has also been proposed to proceed through the two steps (*99*), Eqs. (56) and (57):

$$3LiAlH_4 + 3BX_3 \rightarrow 3LiBH_4 + 3AlX_3 \tag{56}$$

$$3LiBH_4 + BX_3 \rightarrow 2B_2H_6 + 2LiX \tag{57}$$

This proposal is not inconsistent with the one just made. Whether or not the production of diborane proceeds through two distinct steps, rather than a series of steps involving several side reactions, could easily be determined.

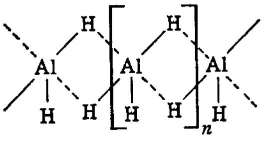
The preparation of $B_2D_6$ has been reported (*72*) by the reaction of boron trifluoride and $LiAlD_4$, while $B_2{}^{10}D_6$ and $B_2{}^{10}H_6$ have been prepared by the reaction of $B^{10}F_3$ and $LiAlD_4$ and $LiAlH_4$ respectively (*69*).

Little success has been reported in the reduction of organohaloboranes to the corresponding organoboranes, although some effort has been made. However, Coates reported the reduction of bis(dimethylamino)chloroborane to bis(dimethylamino)borane, using $LiAlH_4$ in diethyl ether (*21a*).

One of the most important contributions of the Schlesinger group was their convenient, high-yield synthesis of aluminum hydride from $LiAlH_4$ and aluminum chloride in diethyl ether (*3*):

$$3LiAlH_4 + AlCl_3 \rightarrow 4AlH_3 + 3LiCl \tag{58}$$

The isolation of pure aluminum hydride requires rapid addition of the reagents followed by rapid filtration of the by-product lithium chloride. This is necessitated by the fact that aluminum hydride polymerizes and precipitates from solution shortly (within minutes) after the reactants are mixed. Aluminum hydride is believed to polymerize by means of hydrogen bridge bonds in a linear manner (II); however, cross-linking is also possible:



(II)

Although the existence of hydridoaluminum halides has been demonstrated via redistribution of aluminum hydride and aluminum chloride (*139*), it is only recently that these compounds have been identified as intermediates in the above reaction. Ashby and Prather (*6*) studied the reaction of $LiAlH_4$ and aluminum chloride at several stoichiometries, demonstrating a stepwise reaction:

$$LiAlH_4 + 3AlCl_3 \rightarrow 4HAlCl_2 + LiCl \tag{59}$$

$$LiAlH_4 + AlCl_3 \rightarrow 2H_2AlCl + LiCl \tag{60}$$

$$3LiAlH_4 + AlCl_3 \rightarrow 4AlH_3 + 3LiCl \tag{61}$$

The hydridoaluminum halides were detected by infrared analysis and identified by isolation. It is interesting that when the hydride is added to halide, the by-product LiCl (insoluble in diethyl ether) does not precipitate until the stoichiometry is such as to produce $AlH_3$. Apparently in the stoichiometry represented by Eq. (59) the LiCl is complexed to the hydridoaluminum halide as $LiAlCl_3H$. When all of the ether was removed from the solution under vacuum and then readded, the hydridoaluminum halide and LiCl were easily separated. It would appear that when the ether solvent is removed, the LiCl crystallizes into a stable crystalline lattice pattern which does not dissolve when ether is readded to the mixture. This proposal was strengthened by the fact that the solution produced from the reaction represented by Eq. (59) precipitated LiCl when an equimolar amount of triethylamine was added to the solution. Thus, the complex $LiAlCl_3H$ was cleaved according to Eq. (62):

$$LiAlCl_3H + (C_2H_5)_3N \rightarrow LiCl + HAlCl_2{\cdot}N(C_2H_5)_3 \tag{62}$$

Filtration of the precipitated LiCl followed by removal of the ether solution under vacuum produced the hydridoaluminum dichloride as the triethylamine adduct in high yield. This behavior was also observed for the stoichiometry represented by Eq. (60). The reactions of $LiAlH_4$ and $AlBr_3$ and $AlI_3$ were also studied in the manner described for $AlCl_3$. Results similar to those described for the reactions with $AlCl_3$ (Eqs. 59–61) were obtained.

Evans and co-workers (*32*) studied the reaction of $LiAlH_4$ and $AlCl_3$ (and $AlI_3$) conductometrically. They interpreted the first step of this reaction differently from Ashby and Prather. The first steps of the reaction (adding hydride to halide) proposed for $AlCl_3$ and $AlI_3$ are as follows:

$$LiAlH_4 + 2AlCl_3 \rightarrow LiCl + (Al_2Cl_5)^+ + (AlH_4)^- \tag{63}$$

$$LiAlH_4 + 3AlI_3 \rightarrow Li^+ + (Al_2I_7)^- + 2H_2AlI \tag{64}$$

There is some difficulty in rationalizing the stepwise reduction in the above manner. Neither Eq. (63) nor (64) proposes the intermediate formation of $HAlX_2$, yet the infrared spectrum of the resulting reaction mixture (hydride:halide, 1:3) has a strong Al-H absorption band at $5.25\mu$ (*6*). The Al-H bands found for $HAlCl_2$, $H_2AlCl$, and $H_3Al$ are 5.25, 5.40, and $5.60\mu$, respectively. In the first step of the reaction the disappearance of the Al-H band of $LiAlH_4$ ($5.75\mu$) coincides with the appearance of the Al-H band for $HAlCl_2$, and the disappearance of the Al-H band for $HAlCl_2$ ($5.25\mu$) in the second step coincides with the appearance of the Al-H band for $H_2AlCl$ ($5.40\mu$), etc. Thus, the appearance of the Al-H band characteristic of $HAlCl_2$, at the hydride:halide ratio of 1:3, is indicative of a stepwise reduction as expressed by Eqs. (59–61).

Wiberg and Schmidt (*138*) reported that the reaction of $LiAlH_4$ and gallium chloride in diethyl ether at $-30°$ produced gallium aluminum hydride:

$$3LiAlH_4 + GaCl_3 \rightarrow Ga(AlH_4)_3 + 3LiCl \tag{65}$$

The $Ga(AlH_4)_3$ remained in solution at $-30°$; however, at 0° it decomposed to gallium hydride and aluminum hydride:

$$Ga(AlH_4)_3 \rightarrow GaH_3 + 3AlH_3 \tag{66}$$

Gallium hydride, isolated at 20° as $GaH_3 \cdot O(C_2H_5)_2$, decomposed above 35° to gallium metal and hydrogen, releasing the solvated diethyl ether.

Wiberg and Schmidt (*138*) also reported the reaction of $LiAlH_4$ and indium trichloride in diethyl ether solution at −70°:

$$3LiAlH_4 + InCl_3 \rightarrow In(AlH_4)_3 + 3LiCl \qquad (67)$$

The resulting indium aluminum hydride, $In(AlH_4)_3$, precipitated from solution as a white powder. At −40° the $In(AlH_4)_3$ was reported to decompose according to Eq. (68):

$$In(AlH_4)_3 \rightarrow In + H_2 + 3AlH_3 \qquad (68)$$

This behavior is somewhat strange in that indium hydride, prepared from indium chloride and lithium hydride, was reported to be stable to 90°.

These workers also reported the replacement of only one chlorine atom of $InCl_3$ by reaction with $LiAlH_4$ in diethyl ether at 20°:

$$LiAlH_4 + InCl_3 \rightarrow Cl_2InAlH_4 + LiCl \qquad (69)$$

The resulting dichloroindium aluminohydride was reported to be an insoluble white solid stable to 100°.

*e. Group IVA: C, Si, Ge, Sn, Pb.* There are over one hundred reports in the literature concerning the reaction of $LiAlH_4$ with halides of carbon. A discussion of this reaction in detail cannot be given here. However, in general, reduction of halides of carbon with $LiAlH_4$ leads to the formation of hydrocarbons. When diethyl ether is used as a solvent the reductions are slow and yields are poor. If higher boiling solvents such as tetrahydrofuran or dibutyl ether are used, faster reactions and higher (but still relatively poor) yields of reduction product can be obtained. In general the reactivity of halides is $I \geq Br > Cl$ and alkyl groups $1° > 2° > 3°$:

$$4RX + LiAlH_4 \rightarrow 4RH + AlX_3 + LiX \qquad (70)$$

The reaction of $LiAlH_4$ and silicon tetrachloride in diethyl ether was reported to produce silane in essentially quantitative yield (*33, 34*):

$$LiAlH_4 + SiCl_4 \rightarrow SiH_4 + LiCl + AlCl_3 \qquad (71)$$

Silane is a gas and explodes on exposure to air.

Reduction of hexachlorodisilane with $LiAlH_4$ in diethyl ether solution produced disilane in 87% yield (*40*):

$$3LiAlH_4 + 2Si_2Cl_6 \rightarrow 2Si_2H_6 + 3LiCl + 3AlCl_3 \qquad (72$$

Reduction of dialkylaminohalosilanes by $LiAlH_4$ in diethyl ether solution resulted in the formation of silane in 90% yield:

$$(CH_3)_2NSiCl_3 \xrightarrow{LiAlH_4} SiH_4 + H_2 \qquad (73)$$

$$[(CH_3)_2N]_2SiCl_2 \xrightarrow{LiAlH_4} SiH_4 + H_2 \qquad (74)$$

More recently the reduction of silicon tetrachloride by $LiAlH_4$ to silane has been used on an industrial scale as a route to pure silicon for transistors. The silicon for this purpose needs to be $>99.9\%$ pure. Boron trichloride present in silicon tetrachloride is removed by conversion to $LiBH_4$ which is not volatile (*86a*).

The reduction of alkyl- or aryl-substituted silicon halides to the corresponding hydrides with $LiAlH_4$ has been well documented (*30, 40, 92, 93*, and others). In general the reaction proceeds well and in high yield. For example, di-*n*-propyldichlorosilane was reduced to di-*n*-propylsilane in 80% yield and tri(*p*-dimethylaminophenyl)chlorosilane was reduced to tri(*p*-dimethylaminophenyl)silane in 98% yield:

$$2(C_3H_7)_2SiCl_2 + LiAlH_4 \rightarrow 2(C_3H_7)_2SiH_2 + LiCl + AlCl_3 \qquad (75)$$

Finholt and co-workers (*40*) reported the reaction of $LiAlH_4$ and germanium tetrachloride ($GeCl_4$) in diethyl ether. Germane ($GeH_4$) was produced in 30% yield:

$$LiAlH_4 + GeCl_4 \rightarrow GeH_4 + AlCl_3 + LiCl \qquad (76)$$

Sometime later Sujishi and Keith (*101*) reported only 10–15% yield for the same reaction. The germane ($GeH_4$) was accompanied by 85–90% hydrogen. The low yields were attributed to the formation of both $GeCl_2$ and Ge during the reaction. However, using lithium tri-*t*-butoxyaluminohydride, $GeH_4$ was obtained in 70–80% yield.

Macklen (*70*) also studied the reaction of $LiAlH_4$ and $GeCl_4$. He found that yields of $GeH_4$ as high as 40% could be obtained by employing high temperatures. The low yield was attributed to the decomposition of $HGeCl_3$ and the subsequent reduction of $GeCl_2$ by $LiAlH_4$.

The reduction of alkyl- or aryl-substituted germanium halides to the corresponding hydrides with $LiAlH_4$ appears to be well established. *n*-Propyltrichlorogermane has been reduced by $LiAlH_4$ in isopropyl ether to *n*-propylgermane in 85% yield (*110*). Likewise triphenylbromogermane was reduced in 87% yield to triphenylgermane by reduction with $LiAlH_4$ (*63*):

$$4(C_6H_5)_3GeBr + LiAlH_4 \rightarrow 4(C_6H_5)_3GeH + AlBr_3 + LiBr \qquad (77)$$

The reduction of organohalostannanes to organostannanes by $LiAlH_4$ in diethyl ether proceeds well, probably due to the greater stability of organostannanes as compared to stannane. Finholt, Schlesinger, and others (*41, 92, 93*) have reported the $LiAlH_4$ reduction of methyltrichlorostannane, dimethyldichlorostannane, and trimethylchlorostannane to methylstannane, dimethylstannane, and trimethylstannane. Other organohalostannanes were reduced with about the same amount of success; therefore, it appears that the reduction is quite general:

$$R_nSnX_{4-n} \xrightarrow{LiAlH_4} R_nSnH_{4-n} \qquad (78)$$

Later Wiberg and Bauer (*120*) studied the same reaction at −60° in diethyl ether. A white solid precipitated from the reaction mixture which was claimed to be tin aluminum hydride:

$$4LiAlH_4 + SnCl_4 \rightarrow Sn(AlH_4)_4 + 4LiCl \qquad (79)$$

The white solid decomposed at −40° to $H_2$ and $Sn(AlH_4)_2$ or $SnH_4$. Finely divided tin was also produced, indicating decomposition of stannane to tin under the reaction conditions.

*f. Group VA: P, As, Sb, Bi.* Paddock (*84a*) reported the reaction of $LiAlH_4$ and phosphorus trichloride ($PCl_3$) in diethyl ether at 0°. The formation of phosphine ($PH_3$) was reported in good yield:

$$4LiAlH_4 + 3PCl_3 \rightarrow 4PH_3 + 3AlCl_3 + 3LiCl \qquad (80)$$

In diethyl ether solution there is apparently little tendency for the phosphine to be held in solution as $PH_3 \cdot AlCl_3$.

Wiberg and Modritzer (*127*) verified the formation of phosphine in the above reaction at temperatures as low as −100°. At these low temperatures phosphine and hydrogen in equimolar amounts were formed.

Further work with the phosphorus halides was carried out by Wiberg and Muller-Schiedmayer (*134*). They found that reaction of $LiAlH_4$ and phosphorus tribromide ($PBr_3$) in diethyl ether at −30° produced only 10% $PH_3$ and 90% yellow $(PH)_x$. At −115° $H_2$, $(PH)_x$, and $PH_3$ were formed. Interestingly, reaction at −50° gave only $PH_3$. Allowing $PCl_3$ and $LiAlH_4$ to react at −100° resulted in the formation of $PH_3$ and $(PH)_x$. The same workers reported the reaction of $LiAlH_4$ and $POCl_3$ or $POBr_3$ in diethyl ether at −110°. The products were $LiAlO_2$, $H_2$, $PH_3$, and $(PH)_x$ (*135*).

The possible existence of pentavalent phosphorus hydride was investigated by Wiberg and Modritzer by reaction of $LiAlH_4$ and $PCl_5$ in diethyl ether at −100°. The expected $PH_5$ was not formed even at this low temperature; instead, an equimolar mixture of $PH_3$ and $H_2$ was formed.

The reduction of phenyldichlorophosphine by $LiAlH_4$ in diethyl ether to phenylphosphine has been reported by several workers (*45, 61, 111*):

$$C_6H_5PCl_2 \xrightarrow{LiAlH_4} C_6H_5PH_2 \qquad (81)$$

The reaction proceeds well and appears to be a satisfactory method for reducing organohalophosphines to organophosphines.

In two patents (*92, 93*) Schlesinger and Finholt claimed the formation of arsine by the reaction of $LiAlH_4$ and arsenic trichloride ($AsCl_3$):

$$3LiAlH_4 + 4AsCl_3 \rightarrow 4AsH_3 + LiCl + 3AlCl_3 \qquad (82)$$

Later Wiberg and Modritzer (*133*) reported the preparation of arsine in 83% yield by the reaction of $LiAlH_4$ and $AsCl_3$ in diethyl ether at −90°. The same workers also reported the reaction of $LiAlH_4$ with the following arsenic compounds: $C_6H_5AsCl_4$, $(C_6H_5)_2AsCl_3$, $(C_6H_5)_3AsCl_2$, and $(C_6H_5)_4AsBr$ in diethyl ether at temperatures as low as −95° (*130*). The expected $(C_6H_5)_nAsH_{5-n}$ compounds were not formed; instead, the phenyl-substituted trivalent compounds $(C_6H_5)_nAsH_{3-n} + H_2$ were produced in good yield.

Schlesinger and Finholt implied in two patents (*92*, *93*) that $LiAlH_4$ and antimony trichloride ($SbCl_3$) reacted to form stibene ($SbH_3$); however, no details were given. Wiberg and Modritzer later reported (*133*) that $LiAlH_4$ and $SbCl_3$ in diethyl ether at −90° produced $SbH_3$ in 82% yield:

$$3LiAlH_4 + 4SbCl_3 \rightarrow 4SbH_3 + 3AlCl_3 + 3LiCl \qquad (83)$$

The possible existence of pentavalent antimony hydride ($SbH_5$) was explored by Wiberg and Modritzer (*128*). In this connection antimony pentachloride ($SbCl_5$) and $LiAlH_4$ in diethyl ether were allowed to react at −120°. Instead of the expected $SbH_5$, an equimolar mixture of $SbH_3$ and $H_2$ was produced. It was concluded that $SbH_5$, in contrast to $Sb(CH_3)_5$, is not stable even at −120°.

In two patents (*92*, *93*) Finholt and Schlesinger claimed the reduction of organohaloantimony compounds to the corresponding stibenes. No details were given. Further work by Wiberg and Modritzer (*129*) described the reduction of alkyl antimony halides with $LiAlH_4$ in diethyl ether. Attempts to reduce $(CH_3)_3SbBr_2$ and $(CH_3)_4SiI$ at −80° did not produce the expected hydrides. Only $(CH_3)_3Sb$ was isolated and identified. Nor did reduction of phenyl-substituted antimony halides with $LiAlH_4$ produce the expected pentavalent substituted antimony hydrides (*131*). Reduction of $C_6H_5SbCl_4$ and $(C_6H_5)_2SbCl_3$ with $LiAlH_4$ and diethyl ether at temperatures as low as −90° produced only the trivalent antimony hydrides, $C_6H_5SbH_2$ and $(C_6H_5)_2SbH$:

$$(C_6H_5)_nSbX_{5-n} + (5 - n)H^- \rightarrow (C_6H_5)nSb_{3-n} + H_2 + (5 - n)X^- \qquad (84)$$

No reports concerning the reduction of bismuth trichloride with $LiAlH_4$ are available; however, attempted reduction of $(C_6H_5)_3BiCl_2$ with $LiAlH_4$ has been reported by Wiberg and Modritzer (*132*). The products at −95° in diethyl ether solvent were $(C_6H_5)_3Bi$ and $H_2$.

*g. Group VIA: Se, Te.* Van Langen and Plas reported that the reaction of $LiAlH_4$ and $(C_6H_5)_2TeBr_2$, $(C_6H_5)_2SeBr_2$, and $(C_6H_5)_2SeCl_2$ in dioxane at room temperature did not result in the formation of $(C_6H_5)_2TeH_2$ or $(C_6H_5)_2SeH_2$ (*106*). The products were $(C_6H_5)_2Te$ and $(C_6H_5)_2Se$ as well as $AlX_3$, LiX, and $H_2$.

*h. Transition Metal Halides: Ti, Re, Te, Fe, Co.* Two reports by Wiberg and co-workers (*126*, *146*) described the reduction of titanium tetrachloride ($TiCl_4$) using $LiAlH_4$. In diethyl ether at −110°, titanium aluminum hydride, $Ti(AlH_4)_4$, was reported to precipitate from solution. At −85° the $Ti(AlH_4)_4$ decomposed to the elements:

$$LiAlH_4 + TiCl_4 \rightarrow Ti(AlH_4)_4 + 4LiCl \tag{85}$$

$$Ti(AlH_4)_4 \rightarrow Ti + 4Al + 8H_2 \tag{86}$$

Huber and Grosse (*62*) attempted to prepare $(ReH_4)^-$ by reacting $LiAlH_4$ with rhenium trichloride ($ReCl_3$). No $(ReH_4)^-$ was formed, but $H_2$ was evolved and $ReCl_3$ was reduced to metallic Re. Likewise, no evidence for the formation of $(ReH_4)^-$ was established by the reaction of bis(triphenylphosphine)rhenium trichloride and $LiAlH_4$.

Ginsberg and co-workers (*50*) reported a very interesting and unusual finding involving the reaction of $Re_2O_7$ and $LiAlH_4$. The reaction was run in tetrahydrofuran-diethyl ether mixture at room temperature resulting in the formation of $K_2ReH_8$. The $(ReH_8)^=$ ion exhibited strong absorption in the infrared region at 1846 and 735 $cm^{-1}$. The validity of the formula assignment of this compound was based on elemental analyses and NMR spectra.

Schaeffer and co-workers (*91*) reported the reaction of $LiAlH_4$ and ferric chloride in diethyl ether. When $LiAlH_4$ was used in excess, Fe·3Al, LiCl, and $H_2$ were formed. Similar results were obtained in the reduction of cobalt bromide (*100a*). Hydrides of cobalt were not isolated; instead, hydrogen was liberated producing a precipitate containing aluminum and cobalt in 2:1 ratio.

### *3. Metal Alkyls*

The reaction of $LiAlH_4$ and dimethylberyllium in diethyl ether solution has been reported by Schlesinger and co-workers to produce beryllium hydride (*12, 92, 93*):

$$LiAlH_4 + (CH_3)_2Be \rightarrow BeH_2 + LiAlH_3CH_3 \tag{87}$$

Yield data were not given. The product was 50% pure, the impurity being diethyl ether which was held strongly to the beryllium hydride as a solvate. An attempt to prepare ether-free beryllium hydride by the reactions of $(CH_3)_2Be$ and dimethylaluminum hydride, $(CH_3)_2AlH$, resulted in the formation of a Be-H compound from which all of the methyl groups could not be removed. The authors suggested the following equilibrium reaction to account for this:

$$(CH_3)_2AlH + (CH_3)_2Be \rightarrow CH_3BeH + (CH_3)_3Al \tag{88}$$

In one experiment a white solid was isolated that analyzed very close for $CH_3BeH$.

Schlesinger and co-workers (*11*) also studied the reaction of $LiAlH_4$

with other metal alkyls. In this connection Zn, Cd, Mg, and Li alkyls were found to produce the corresponding hydrides:

$$2LiAlH_4 + (CH_3)_2Zn \rightarrow ZnH_2 + 2LiAlH_3CH_3 \quad (89)$$

$$2LiAlH_4 + (CH_3)_2Cd \rightarrow CdH_2 + 2LiAlH_3CH_3 \quad (90)$$

$$2LiAlH_4 + (C_2H_5)_2Mg \rightarrow MgH_2 + 2LiAlH_3CH_3 \quad (91)$$

$$LiAlH_4 + CH_3Li \rightarrow LiH + LiAlH_3CH_3 \quad (92)$$

The zinc and cadmium hydrides were obtained ether-free, whereas the beryllium and magnesium hydrides could not be separated from the last traces of diethyl ether. Of the nonalkali metal hydrides, magnesium hydride was the most stable, next beryllium hydride (dec. 125°), then zinc hydride (decomposes slowly at room temperature), and least stable was cadmium hydride (decomposes rapidly at 0°).

An interesting thing about the reaction of $LiAlH_4$ and diethylmagnesium was that the nature of the major product was changed by the mode of addition. When $LiAlH_4$ was added to an excess of diethylmagnesium in diethyl ether, $MgH_2$ precipitated. However, when diethylmagnesium was added to an excess of $LiAlH_4$ in diethyl ether, a clear solution was produced. When the diethyl ether was removed under vacuum to produce a concentrated solution and then benzene added, a white solid precipitated. Analysis indicated a compound of the formula $HMgAlH_4$; however, the authors felt that the solid could be an equimolar mixture of $MgH_2$ and $AlH_3$. Since $MgH_2$ and $AlH_3$ both precipitate from diethyl ether quite readily, it would appear that the precipitated solid probably is $HMgAlH_4$. More investigation in this area might prove both interesting and fruitful.

Attempts by Schlesinger and others (*12*, *12a*) to prepare mercury hydride by the reaction of $LiAlH_4$ with mercury alkyls or aryls at temperatures as low as −80° resulted in the formation of mercury and hydrogen:

$$(C_6H_5)_2Hg \xrightarrow{LiAlH_4} Hg + H_2 + C_6H_6 \quad (93)$$

Schlesinger and co-workers (*12*) also found that reaction of trimethylborane or trimethylaluminum with $LiAlH_4$ resulted in the formation of dimethylaluminum hydride:

$$LiAlH_4 + (CH_3)_3B \rightarrow (CH_3)_2AlH + LiBH_3CH_3 \quad (94)$$

$$LiAlH_4 + (CH_3)_3Al \rightarrow (CH_3)_2AlH + LiAlH_3CH_3 \quad (95)$$

### *4. Metal Hydrides*

Possibly the most fascinating and original contribution in the hydride area since the report announcing the preparation of the first complex metal hydride comes from the laboratory of E. Wiberg in Munich. Wiberg and his students reported (*148a*) the preparation of the first "triple metal hydrides," i.e., complex metal hydrides containing three different metals. They found, for example, that $LiAlH_4$ in tetrahydrofuran or diethyl ether reacted with diborane according to the following stoichiometries:

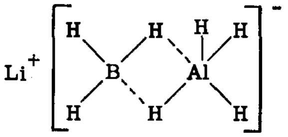
$$LiAlH_4 + 1/2B_2H_6 \rightarrow LiAlH_4 \cdot BH_3 \quad (96)$$

$$LiAlH_4 + B_2H_6 \rightarrow LiAlH_4 \cdot 2BH_3 \quad (97)$$

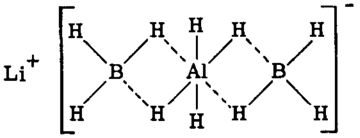
$$LiAlH_4 + 3/2B_2H_6 \rightarrow LiAlH_4 \cdot 3BH_3 \quad (98)$$

$$LiAlH_4 + 2B_2H_6 \rightarrow LiAlH_4 \cdot 4BH_3 \quad (99)$$

Although these triple metal hydrides were represented by the formula $LiAlH_4 \cdot nBH_3$, they could as well be represented by the formula $LiAlH_{4-n}(BH_4)_n$. The amazing thing about these compounds is their reported thermal stability. $LiAlH_4 \cdot 2BH_3$ is reported to be stable to 200° and $LiAlH_4 \cdot BH_3$ to 300°. The structures proposed for these hydrides by Wiberg are represented below:



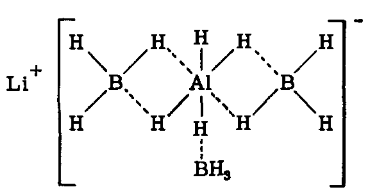
$(LiAlH_4 \cdot BH_3)$



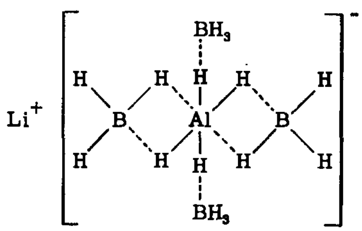
$(LiAlH_4 \cdot 2\,BH_3)$

The unusual stability of these compounds was explained on the basis of aluminum and boron being in their maximum coordination state (at least for $LiAlH_4 \cdot 2BH_3$), i.e., six for aluminum and four for boron. Additional stability was also explained on the basis of the double hydrogen bridge systems formed.

It was found that $LiAlH_4 \cdot 3BH_3$ and $LiAlH_4 \cdot 4BH_3$ evolved diborane at temperatures below 0°. The structures Wiberg proposed for these compounds are presented below:

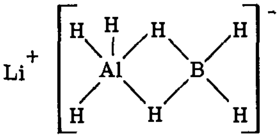


$(LiAlH_4 \cdot 3\,BH_3)$



$(LiAlH_4 \cdot 4\,BH_3)$

When $LiAlH_4 \cdot 4BH_3$ was allowed to warm from −50° to −25°, diborane was evolved and the new hydride, $LiAlH_4 \cdot 3BH_3$, formed. At 0° $LiAlH_4 \cdot 3BH_3$ evolved diborane and formed the stable $LiAlH_4 \cdot 2BH_3$. The decreased stability of $LiAlH_4 \cdot 3BH_3$ and $LiAlH_4 \cdot 4BH_3$ as compared to $LiAlH_4 \cdot 2BH_3$ and $LiAlH_4 \cdot BH_3$ was explained on the basis of the necessity of attaching the additional $BH_3$ units to the molecule by a single hydrogen bridge bond as compared to a more stable double hydrogen bridge bond. Similar type compounds and behavior were reported for other complex metal hydride-diborane systems, e.g., $Ca(AlH_4)_2 n \cdot BH_3$, $NaAlH_4 \cdot nBH_3$, etc. Some effort was made to prove that $LiAlH_4 \cdot BH_3$ and $LiBH_4 \cdot AlH_3$ are not the same compounds.



The latter compound was prepared independently from $LiBH_4$ and $AlH_3$ and was shown to have different thermal stability, specific conductance, solvation tendency, and reaction tendency with diborane than $LiAlH_4 \cdot BH_3$:

$$LiAlH_4 \cdot BH_3 + B_2H_6 \rightarrow LiAlH_4 \cdot 4BH_3 \quad (100)$$

$$LiBH_4 \cdot AlH_3 + B_2H_6 \rightarrow LiBH_4 \cdot AlH_3 \cdot BH_3 \quad (101)$$

Although it seems perfectly reasonable that the compounds reported by Wiberg could originate from the reaction of $LiAlH_4$ and diborane, the evidence is sketchy at best. When $LiAlH_4$ and diborane were allowed to react only two criteria were used to identify the products: (1) complete analysis of the reaction mixture, and (2) determination of the thermal stability of the reaction products. If $LiAlH_4$ and $n$ moles of diborane are mixed in tetrahydrofuran ($B_2H_6 + THF \rightarrow 2BH_3 \cdot THF$, diborane reacts with THF to form nonvolatile $BH_3 \cdot THF$), it is not surprising that the reaction product analyzes for $LiAlH_4 \cdot nBH_3$ since this represents the stoichiometry of addition. The difference in thermal stability of the products as compared to the reactants is certainly evidence of reaction, but not necessarily to the products proposed. No effort was made to fractionally crystallize the products in order to determine whether or not they are true single compounds or a mixture of products.

Possibly the most confusing data reported for these compounds are the thermal stabilities. Can metal hydrides such as $LiAlH_4$ (decomposing at 120°) and $BH_3$ (decomposing at $<100°$) be held together by weak hydrogen bridge bonds (5–15 kcal bonds), be they single or double, and be stable to 200° and 300°? $LiBH_4 \cdot BH_3$ is similar to the compounds in question and dissociates to $LiBH_4 + 1/2B_2H_6$ at 60°. Wiberg also reported the preparation $2LiAlH_4 \cdot AlH_3$; this compound dissociates at room temperature. Another question to ask is why do $LiAlH_4 \cdot 3BH_3$ and $LiAlH_4 \cdot 4BH_3$ release diborane below 0° when $LiAlH_4 \cdot 2BH_3$ and $LiAlH_4 \cdot BH_3$ are stable to such high temperatures? Can the difference between single hydrogen bridge bonds and double hydrogen bridge bonds be so great? It wouldn't appear so. In conclusion, it would appear reasonable that $LiAlH_4$ and diborane do react to form the compounds suggested by Wiberg; however, the claim does not seem adequately substantiated. The thermal stability reported for these compounds seems untenable. It is of interest to consider the report by Schlesinger and Finholt (*93*) that $LiAlH_4$ and $B_2H_6$ react according to the following equation:

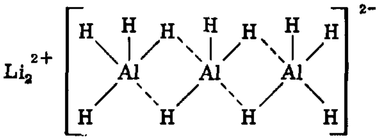
$$LiAlH_4 + 2B_2H_6 \rightarrow LiBH_4 + Al(BH_4)_3 \qquad (102)$$

More work is needed in this area to establish the existence of "triple metal hydrides" and to investigate the unusual thermal stability noted for these compounds.

Wiberg and co-workers (*148a*) studied complex formation between $LiAlH_4$ and aluminum hydride. For example, $2LiAlH_4{\cdot}AlH_3$ was prepared by the reaction of $LiAlH_4$ and aluminum bromide:

$$11LiAlH_4 + AlBr_3 \rightarrow 4[2(LiAlH_4){\cdot}AlH_3] + 3LiBr \qquad (103)$$

Definite evidence for this compound in solution was acquired through conductometric titration. The compound was isolated at low temperature and found to analyze correctly for $Li_2Al_3H_{11}$. The compound decomposed slowly at room temperature, even in the absence of light. The structure proposed for this compound exhibits all three aluminum atoms in the pentavalent state:



$2\,LiAlH_4{\cdot}AlH_3$

Conductometric titrations of solutions of $LiAlH_4$ and $AlBr_3$ indicated the formation of $LiAlH_4{\cdot}nAlH_3$ compounds (where $n = 1, 2, 3,$ or $4$); however, these compounds could not be isolated even at low temperatures due to their instability.

Another route to triple metal hydrides was reported by Wiberg and Neumeier (*136*, *137*). Reaction of lithium hydride and aluminum borohydride was reported to produce $LiAl(BH_4)_3H$ in good yield.

$$LiH + Al(BH_4)_3 \rightarrow LiAl(BH_4)_3H \qquad (104)$$

The product was reported to be stable to 90° whereas $LiAlH_4{\cdot}3BH_3$ was reported to release diborane above 0°. When $LiAl(BH_4)_3H$ was treated with diborane the following reaction occurred:

$$LiAl(BH_4)_3H + 1/2B_2H_6 \rightarrow LiAl(BH_4)_4 \qquad (105)$$

This product was claimed to be the same as the product obtained from the reaction of $LiAlH_4 + 2B_2H_6$.

Another interesting report by Wiberg and co-workers (*148a*) involves the metathetical exchange reaction between two different complex metal hydrides. For example, when $LiAlH_4$ and magnesium borohydride were allowed to react in tetrahydrofuran, lithium borohydride ($LiBH_4$) was said to precipitate, leaving magnesium aluminum hydride in solution:

$$2LiAlH_4 + Mg(BH_4)_2 \rightarrow 2LiBH_4 + Mg(AlH_4)_2 \qquad (106)$$

One difficulty in rationalizing these results lies in the fact that $LiBH_4$ is more soluble in tetrahydrofuran than is $Mg(AlH_4)_2$.

### 5. *Halogens*

Wiberg and Lacal (*126a*) reported the reaction of $LiAlH_4$ and iodine in diethyl ether at −100°. Two moles of hydrogen were liberated per mole of $LiAlH_4$ and $LiAlI_4$ was isolated as a white solid. The quantitative determination of $LiAlH_4$ in diethyl ether solution was reported by Felkin (*35*), using iodometric titration. The reaction was represented as originally reported by Wiberg:

$$LiAlH_4 + 2I_2 \rightarrow 2H_2 + LiI + AlI_3 \qquad (107)$$

Later (*64*) Klanberg and Kohlschutter reported that reaction of $LiAlH_4$ and iodine at −196° produced $LiAl_2I_7$:

$$2LiAlH_4 + 4I_2 \rightarrow LiAl_2I_7 + 4H_2 + LiI \qquad (108)$$

A similar reaction was reported for $LiAlH_4$ and bromine resulting in the formation of $LiAl_2Br_7$. Although these latter results do not agree with those reported by Wiberg and Felkin, they were based on the isolation and identification of $LiAl_2I_7$ and $LiAl_2Br_7$.

### 6. *Halogen Acids*

Reaction of $LiAlH_4$ with halogen acids would be expected to be violent and to liberate hydrogen. Ruff and Hawthorne (*88*) used the reaction of $LiAlH_4$ with tertiary amine salts of halogen acids to advantage to produce a number of amine-alanes in high yield. The reactions were run in diethyl ether as a solvent at temperatures of −30° to 25°:

$$LiAlH_4 + R_3N{\cdot}HCl \rightarrow AlH_3{\cdot}NR_3 + LiCl + H_2 \qquad (109)$$

Dialkylaminoalanes were also prepared by the reaction of $LiAlH_4$ and dialkylammonium chlorides:

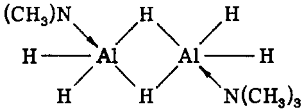
$$LiAlH_4 + R_2NH{\cdot}HCl \rightarrow R_2NAlH_2 + LiCl + H_2 \qquad (110)$$

Formation of the intermediate dialkylamine-alane was indicated at −40°;

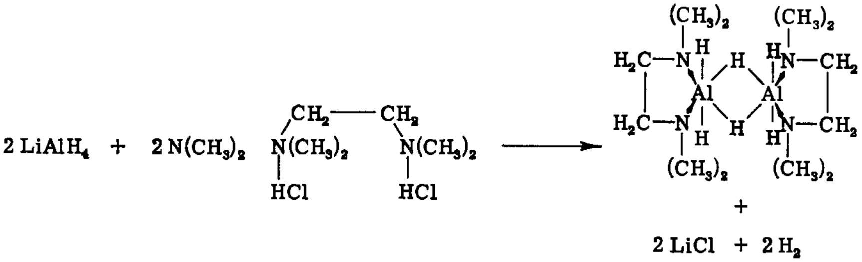
however, at −10° an additional mole of $H_2$ was liberated generating the dialkylaminoalanes:

$$R_2NH{\cdot}AlH_3 \rightarrow R_2N\text{-}AlH_2 + H_2 \qquad (111)$$

These authors presented molecular association data for the amine-alanes and dialkylaminoalanes in benzene solution. The degree of association was 1.4 for trimethylamine-alane; however, this value approached 1.0 as the steric requirement of the tertiary amine increased. The structure proposed for trimethylamine-alane dimer involves hydrogen bridge bonds (although no evidence for hydrogen bridge bonds was found in the infrared spectra):



Davidson and Wartik (*25*) employed the same type of reaction used by Ruff and Hawthorne to prepare an unusually stable tertiary amine-alane. These workers allowed $LiAlH_4$ and *N,N,N′,N′*-tetramethylethylenediamine dihydrochloride to react and isolated the expected amine-alane. This amine-alane is unusual with respect to its reported thermal stability. Whereas all known amine-alanes decompose rapidly at 100°, this amine-alane is stable even at 140°. The compound is reported to be dimeric and the structure proposed involves hexavalent aluminum.



(112)

## 7. *Olefins*

The reaction of $LiAlH_4$ with olefins can proceed to produce two different types of product depending on the reaction conditions. On the one hand, $LiAlR_4$ compounds can be produced and, on the other hand, polymerization of the olefin can be effected.

Zeigler (*155*) has reported the reaction of ethylene and $LiAlH_4$ at 100°. The product formed, employing excess ethylene, was $LiAl(C_2H_5)_4$:

$$LiAlH_4 + 4(CH_2{=}CH_2) \rightarrow LiAl(C_2H_5)_4 \qquad (113)$$

Later Fulton (*46*) reported the reaction of $LiAlH_4$ with several olefins using $AlCl_3$ as a catalyst. High yields of $LiAlR_4$ compounds were reported. Aluminum alkyls were generated from the $LiAlR_4$ compounds by reaction with $AlCl_3$:

$$LiAl(n\text{-}C_3H_7)_4 \xrightarrow{AlCl_3} Al(n\text{-}C_3H_7)_3 \qquad (114)$$

Fulton (*46*) also reported the preparation of $LiAlR_4$ compounds from $LiAlH_4$ and olefins. High yields (90–100%) were reported when the reaction was run in the presence of certain metal halides such as KI, $HgCl_2$, NaCl, and others.

In a period of 3 years (1957–1960) over seventeen patents have issued, describing the polymerization of olefins using a catalyst system composed of $LiAlH_4$ and a number of transition metal halides (*1*, *23*, *24*, *26*, *27*, *48*, *78*, *81–84a*, *86*, *102–105*, *112*). Polyethylene, polypropylene, polycyclopentadiene, etc., have been prepared using this catalyst system. The co-catalyst used most was $TiCl_4$; however, many other transition metal halides were described, such as those of Zr, Cr, Mo, Hf, etc. It appears that $LiAlH_4$ is serving the same function as an aluminum alkyl (the normal Ziegler catalyst combination is $(C_2H_5)_3Al + TiCl_4$) in the catalysis. Under the conditions of the reaction, $LiAlH_4$ should be converted to $LiAlR_4$ or $AlR_3$.

### 8. *Metal or Metalloid Esters*

Although reports in the literature are numerous concerning the reduction of metal and metalloid halides by $LiAlH_4$, there are only four reports concerning the reduction of metal or metalloid esters. In general, reduction of esters has been considered to be more difficult than the corresponding halides. For this reason and because sodium borohydride has been reported not to react with methyl borate, it has been assumed that esters are unreactive toward complex metal hydrides.

The first report of the reduction of a metal-alkoxy compound by any complex metal hydride was made by Gilman and Branner (*49*). They reported the reduction by $LiAlH_4$ of tris(1-naphthyl)ethoxysilane to tris-(1-naphthyl)silane. Later Hawthorne (*56*) reported the reduction of diethylphenylboronate in pyridine using $LiAlH_4$:

$$C_6H_5B(OC_2H_5)_2 + LiAlH_4 \xrightarrow{Py} C_6H_5BH_2\cdot Py \qquad (115)$$

Kollonitsch (*65*), in one sentence, reported that the reaction of $LiAlH_4$ and isopropyl borate resulted in the formation of $LiBH_4$:

$$LiAlH_4 + B(O\text{-}i\text{-}Pr)_3 \rightarrow LiBH_4 + Al(O\text{-}i\text{-}Pr)_3 \qquad (116)$$

Sometime later Ashby (*5*) studied the reduction of several borate esters, using $NaBH_4$, $LiAlH_4$, and $NaAlH_4$ in a number of complexing solvents. Although $NaBH_4$ did not reduce borate esters in ether-type solvents, even under forcing conditions, $LiAlH_4$ and $NaAlH_4$ did reduce borate esters readily at room temperature. Lithium aluminum hydride and phenyl borate reacted to form $LiBH_4$, provided the borate ester was added to the $LiAlH_4$. This reaction does not appear to be general for all borate esters since reaction of $LiAlH_4$ and methyl borate produced a number of products that were not easily identified. If the mode of addition is reversed (that is, $LiAlH_4$ added to phenyl borate), instead of $LiBH_4$, diborane is produced in 47% yield:

$$3LiAlH_4 + 4B(OC_6H_5)_3 \rightarrow 2B_2H_6 + 3LiAl(OC_6H_5)_4 \qquad (117)$$

The low yield of diborane is due to a side reaction involving diborane and $LiAlH_4$:

$$LiAlH_4 + 1/2B_2H_6 \rightarrow LiBH_4 + AlH_3 \qquad (118)$$

Not only was $LiBH_4$ detected and isolated as a by-product, but also $LiB_2H_7$, formed by the reaction of $LiBH_4$ and diborane:

$$LiBH_4 + 1/2B_2H_6 \rightarrow LiB_2H_7 \qquad (119)$$

Thus, if diborane is desired as the product from this reaction, $LiAlH^4$ should be added slowly to the borate ester in order to minimize reaction of the resulting diborane with $LiAlH_4$ and $LiBH_4$. If $LiBH_4$ is the desired product, then the borate ester should be added to $LiAlH_4$. Side reactions can be decreased by using a tertiary amine solvent. Diborane formed in the reaction is immediately complexed to form the amine-borane which is much more stable toward reaction with $LiAlH_4$ and $LiBH_4$ than free diborane. The yield of amine-borane was 77% when $LiAlH_4$ and phenyl borate were allowed to react in triethylamine solvent.

Once again the results were not the same with methyl borate as with phenyl borate. Addition of $LiAlH_4$ to methyl borate in diethyl ether did not result in the evolution of diborane. Instead, $LiBH_4$ and $LiB_2H_7$ were the major products. However, in triethylamine solvent triethylamine-borane was formed in 68% yield:

$$3LiAlH_4 + 4B(OCH_3)_3 \xrightarrow{(C_2H_5)_3N} 4BH_3{\cdot}N(C_2H_5)_3 + 3LiAl(OCH_3)_4 \qquad (120)$$

Thus it appears that $LiAlH_4$ is much more reactive toward B-OR compounds than $NaBH_4$, and that reaction is very facile with $LiAlH_4$, producing at room temperature $LiBH_4$ or $B_2H_6$ depending on the mode of addition and the nature of the solvent.

Although methyl borate could not be made to react with $NaBH_4$, phenyl borate did react at 200° when triethylamine was used as the solvent.

### 9. *Solvates of* $LiAlH_4$

Wiberg and Gosele (*122a*) first studied the formation of solvates of $LiAlH_4$ with strongly complexing solvents. In diethyl ether at −60°, $LiAlH_4$ formed a bis-etherate. The vapor pressure was 38 mm at 0°. This solvate lost ether under vacuum at room temperature producing the mono-etherate:

$$LiAlH_4 + n(C_2H_5)_2O \xrightarrow{-60^\circ} LiAlH_4 \cdot 2(C_2H_5)_2O \xrightarrow[\text{(vac.)}]{25^\circ} LiAlH_4 \cdot (C_2H_5)_2O + (C_2H_5)_2O \quad (121)$$

In tetrahydrofuran at −20°, $LiAlH_4$ formed a bis-tetrahydrofuranate which was soluble not only in diethyl ether and tetrahydrofuran, but also in benzene. The vapor pressure was 40 mm at 40°. At 30°–40°, 1 mole of tetrahydrofuran was evolved from the bis-solvate producing the mono-solvate. This compound was also found to be soluble in diethyl ether and tetrahydrofuran, but not in benzene. Its vapor pressure is only 1 mm at 40°.

$$LiAlH_4 + n(\text{THF}) \xrightarrow{-20^\circ} LiAlH_4 \cdot 2\text{THF} \xrightarrow{30^\circ\text{–}40^\circ} LiAlH_4 \cdot \text{THF} + \text{THF} \quad (122)$$

In triethylamine, $LiAlH_4$ was reported to form a tris-aminate at −80°. At −40°, however, triethylamine was evolved and the bis-aminate formed. At 0° more triethylamine was evolved and the mono-aminate formed. It was reported that the mono-aminate was stable to 180°, which represents unusual stability as compared to the unsolvated compounds which decompose at 90°.

The formation of a bis-tetrahydrofuranate of $LiAlH_4$ was verified by Hollingsworth and co-workers (*52*). The solvate was prepared by displacing diethyl ether from $LiAlH_4 \cdot n(C_2H_5)_2O$ in tetrahydrofuran solvent. Establishment of the new solvate was made by a new technique involving vapor phase chromatography. The same workers (*20*) also presented evidence for the stability of $LiAlH_4 \cdot (C_2H_5)_2O$ at 25° by vapor pressure measurements and reported the solubility of $LiAlH_4$ in diethyl ether (40 gm/100 gm solvent) to be considerably higher than previously reported. A further report by Hollingsworth and co-workers (*60*) established the formation of THF solvates of $LiAlH_4$ and several of its alkoxy derivatives $[LiAlH_n(OR_{4-n})]$. In most cases the mono-solvate was formed. In some cases, where an increasing number of hydrogen atoms in $LiAlH_4$ were replaced by OR groups, the solvate value was less than one.

## IV. Sodium Aluminum Hydride

Less information is available for $NaAlH_4$ or the other complex aluminum hydrides than for $LiAlH_4$. The reason is that $LiAlH_4$ is more readily prepared from LiH and $AlCl_3$ than $NaAlH_4$ from NaH and $AlCl_3$ and therefore, until recently, only $LiAlH_4$ was commercially available. The high solubility of $LiAlH_4$ in diethyl ether will always make $LiAlH_4$ the complex metal hydride of choice in certain reduction reactions; however, with the new direct route to complex metal hydrides, $NaAlH_4$ is prepared more conveniently and much more economically than $LiAlH_4$. It is presumed from the availability standpoint that in the future more work will be done with $NaAlH_4$ and more information will be forthcoming. In general it appears that $NaAlH_4$ can be prepared by essentially the same methods described for the preparation of $LiAlH_4$ and that reactions of $NaAlH_4$ are essentially the same as with $LiAlH_4$.

### A. PROPERTIES AND STRUCTURE

Sodium aluminum hydride ($NaAlH_4$) is a white crystalline solid stable to dry air at room temperature, but very susceptible to moisture and protic solvents. Sodium aluminum hydride is essentially insoluble in diethyl ether; however, it is very soluble in tetrahydrofuran and diglyme. Solutions of $NaAlH_4$ in either tetrahydrofuran or diglyme appear to be stable for at least several months, if not exposed to air.

Russian workers (*28*) have investigated the thermal stability of $NaAlH_4$ by differential thermal analysis. The following temperatures and corresponding thermal effects were observed:

| | |
|---|---|
| 178° | fusion of $NaAlH_4$ |
| 290°–298° | decomposition according to: $NaAlH_4 \rightarrow NaH + Al + 3/2H_2$ |
| 422°–432° | decomposition of NaH according to: $NaH \rightarrow Na + 1/2H_2$ |
| 660°–664° | fusion of aluminum metal |

As was discussed earlier (Section III,A) when considering the decomposition of $LiAlH_4$, one cannot describe the decomposition products with any degree of certainty unless they are isolated and identified. There appears to be general agreement that $NaAlH_4$ is stable to ~180° and that the nature of the decomposition products is unknown.

Seidl (*97*) studied the crystal structure of $NaAlH_4$ and found its symmetry to be of the tetragonal-bipyramidal and tetragonal-pyramidal class. From the X-ray measurement the most probable space group is $I4_1$ or $I4_1/a$ and the lattice constants $a = 5.02$, $c = 11.31$ Å; $c/a = 2.253$. The elementary cell was reported to contain 4 molecules. If the space group is $I4_1/a$, then $NaAlH_4$ possesses a tetrahedral arrangement; however, if the space group is $I4_1$, it cannot be said that the structure is tetrahedral. More work needs to be done to conclusively establish the structure of $NaAlH_4$. It would be reasonable in the meantime to assume that the structure is similar to $LiAlH_4$, which is believed to be tetrahedral.

### B. PREPARATIONS

Sodium aluminum hydride was first reported in 1951 by Schlesinger and Finholt (*92*), the same workers to first prepare $LiAlH_4$. This complex metal hydride was prepared in 60% yield by the reaction of sodium hydride and aluminum bromide in dimethyl ether:

$$4NaH + AlBr_3 \rightarrow NaAlH_4 + 3NaBr \qquad (123)$$

The product was isolated by filtration of the insoluble NaBr, followed by evaporation of the dimethyl ether leaving the solid $NaAlH_4$.

Finholt (*37*) later reported two improved methods for the preparation of $NaAlH_4$. The first method reported in 1957 involved the preparation of aluminum hydride from $LiAlH_4$ and aluminum chloride followed by reaction of a tetrahydrofuran solution of the aluminum hydride with sodium hydride. Sodium aluminum hydride was produced in 93% yield:

$$3LiAlH_4 + AlCl_3 \xrightarrow{Et_2O} 4AlH_3 + 3LiCl \qquad (124)$$

$$AlH_3 + NaH \xrightarrow{THF} NaAlH_4 \qquad (125)$$

The advantages of this process over the direct reaction of NaH and an aluminum halide are based on higher yield, higher purity product, and ease of reaction.

The second process improvement reported by Finholt (*38*, *43*) involved a similar two-step reaction in which no $LiAlH_4$ was involved:

$$3NaAlH_4 + AlCl_3 \xrightarrow{THF} 4AlH_3 + 3NaCl \qquad (126)$$

$$4AlH_3 + 4NaH \rightarrow 4NaAlH_4 \qquad (127)$$

The process uses either tetrahydrofuran or the dimethyl ether of ethylene glycol as the solvent. Reaction of $NaAlH_4$ proceeds readily in either solvent, and the subsequent reaction of the product of the first step with NaH also proceeds well due to the solubility of the intermediate $AlH_3$. Since yields are 98%, it is possible to recycle 75% of the product in order to maintain the cyclic process.

Several other reports have appeared in the literature describing the reaction of NaH and $AlCl_3$ as a route to $NaAlH_4$. These reports describe slightly different conditions than have been described thus far in order to improve the yield, rate of reaction, etc. For example, Vit and co-workers (*107*, *108*) claimed the preparation of 99% pure $NaAlH_4$ by the reaction of NaH in an ether-type solvent and $AlBr_3$ in a noncomplexing solvent. Hinckley and Del-Guidise (*57*) described the same reaction using a mineral oil-tetrahydrofuran mixture as a solvent.

Zakarkin and Gavrilenko (*151*) described a substantial process improvement by using triethylaluminum as a catalyst. One of the problems causing slow reaction between NaH and $AlCl_3$ is the insoluble nature of NaH, complicated further by the precipitation of by-product NaCl on the surface of the NaH during the reaction. The triethylaluminum catalyst serves to solubilize the NaH by forming $NaAl(C_2H_5)_3H$, which is soluble in the reaction media and reacts readily with $AlCl_3$ to form $NaAlH_4$ and regenerate the catalyst:

$$NaH + (C_2H_5)_3Al \rightarrow NaAl(C_2H_5)_3H \qquad (128)$$

$$4NaAl(C_2H_5)_3H + AlCl_3 \rightarrow NaAlH_4 + 3NaCl + 3(C_2H_5)_3Al \qquad (129)$$

More recently $NaAlH_4$ has been prepared by direct synthesis from the elements. This method, first reported by Ashby (*2*), involves the reaction of sodium metal, aluminum powder, and hydrogen in tetrahydrofuran or hydrocarbon solvent at moderate temperature and pressure:

$$Na + Al + 2H_2 \rightarrow NaAlH_4 \qquad (130)$$

Sodium aluminum hydride was formed in 99% yield and 99% purity by reaction at 140°C and 5000 psi in toluene, using triethylaluminum as a catalyst. The product is isolated by simply filtering the product from the hydrocarbon diluent. It is best to store $NaAlH_4$ wet with toluene. This preserves the reactivity more than if the solid is stored dry. Storing very reactive solids damp with solvent is widely used in order to maintain reactivity of the solid. For this reason and others NaH is sold as a slurry in 50% mineral oil. The reaction works equally well when tetrahydrofuran is used as the solvent or if sodium metal is replaced by NaH. In tetrahydrofuran solvent the product is isolated from solution by solvent evaporation or benzene precipitation.

The same reaction was reported later by Clasen (*21*) and Zakharkin and Gavrilenko (*153*) with essentially the same results except that poorer yields were reported, 50–87%. These workers performed the reaction in a ball mill over extended periods of time (10–20 hours) in order to activate the aluminum powder.

It is this direct route to $NaAlH_4$ that should increase the use of complex metal hydrides considerably on a commercial scale. Due to the high cost of lithium in any form, $LiAlH_4$ will always be expensive. The raw material cost for preparing $NaAlH_4$ by the direct process adds up to less than 50 cents a pound. The process is simple enough that the cost of $NaAlH_4$ could come within the reach of being used in many commercial processes. In the laboratory, in addition to being a versatile reducing agent, $NaAlH_4$ excels in the treatment of hydrocarbons, ethers, tertiary amines, etc., for drying and purification purposes prior to distillation.

Several process improvement patents have issued recently (*9, 10, 85*) concerning the direct route to $NaAlH_4$. The modifications employed appear to be minor in nature and result.

Several other interesting routes to $NaAlH_4$ have been reported. Although these routes could not compete with the direct synthesis as a convenient or economic route to $NaAlH_4$, they do provide some interesting chemistry. For example, Zakharkin and Gavrilenko (*152*) have reported the preparation of $NaAlH_4$ from $LiAlH_4$ and NaH:

$$LiAlH_4 + NaH \rightarrow NaAlH_4 + LiH \tag{131}$$

The reaction produced $NaAlH_4$ in 90% yield using tetrahydrofuran as a solvent. Ruff and Hawthorne (*89*) reported a convenient route to $NaAlH_4$ and other complex metal hydrides based on the reaction of an amine-alane and metal hydride:

$$AlH_3 \cdot N(CH_3)_3 + NaH \rightarrow NaAlH_4 + N(CH_3)_3 \tag{132}$$

This method possesses even greater importance for the preparation of complex metal hydrides not as readily prepared by the direct synthesis, such as $CsAlH_4$ or $Ca(AlH_4)_2$.

Good and Batha (*51*) reported a preparation of $NaAlH_4$ not intended as a recommended synthesis, but as a means of converting a by-product from another synthesis to something useful. In preparing diborane from NaH, $AlCl_3$, and $BCl_3$, sodium tetrachloroaluminate ($NaAlCl_4$) was produced as a by-product. The $NaAlCl_4$ was then converted to $NaAlH_4$ by reaction with NaH in tetrahydrofuran. Sodium aluminum hydride was produced in 40% yield:

$$12NaH + 3AlCl_3 + 4BCl_3 \rightarrow 2B_2H_6 + 3NaAlCl_4 + 9NaCl \tag{133}$$

$$NaAlCl_4 + 4NaH \rightarrow NaAlH_4 + 4NaCl \tag{134}$$

Since diborane was the desired product in the process, the $NaAlH_4$ produced according to Eq. (134) was used to produce more diborane by reaction with $BCl_3$.

## C. REACTIONS

In general not many reactions involving $NaAlH_4$ have been reported. This is due to two factors: (1) $NaAlH_4$ has not been readily available (as has, for example, $LiAlH_4$), and (2) $NaAlH_4$ is known to react similarly to $LiAlH_4$ with respect to reaction rate, product yield, etc. Finholt *et al.* (*42*), for example, observed little difference in the reduction of thirteen organic compounds with respect to reaction rate and product yield while comparing $LiAlH_4$ and $NaAlH_4$. Also, Prochayka and co-workers (*108*) studied the reduction of thirteen nonorganic functional compounds using $NaAlH_4$ ($BCl_3$, $AlCl_3$, $SiCl_4$, $SnCl_4$, $PCl_3$, $AsCl_3$, $SbCl_3$, $B(OCH_3)_3$, $P(OC_2H_5)_3$, $CO_2$, $CS_2$, and $I_2$) and found the results generally the same as with $LiAlH_4$. The following reactions describe the known chemistry of $NaAlH_4$ and bear testimony to the similarity of this compound as a reducing agent to $LiAlH_4$.

Zakharkin and co-workers (*154*) reported the reduction of $HSiCl_3$ by $NaAlH_4$ in $(CH_2OCH_3)_2$ at $-50°$ to produce silane ($SiH_4$) in 100% yield. These workers also reported that the reduction of $SiCl_4$ or $Si(OC_2H_5)_4$ with

$NaAlH_4$ produced $SiH_4$, and $GeCl_4$ or $Ge(OC_2H_5)_4$ produced $GeH_4$. Mason and Kelley (*71a*) reported that the reduction of $SiCl_4$ to $SiH_4$ by $NaAlH_4$ in tetrahydrofuran provides an excellent method for obtaining a boron-free product.

Finholt and co-workers (*44*) studied the reaction of $NaAlH_4$ and ammonia, phosphine ($PH_3$), and arsine ($AsH_3$). The results were similar to those reported for reaction with $LiAlH_4$ (Section III,C,1,b). It was possible under the proper conditions to prepare and isolate $NaAl(NH_2)_4$ from $NaAlH_4$ and ammonia.

Ashby, Robinson, and co-workers (*7*, *31*) and Clasen (*21*) have described metathetical exchange reactions involving $NaAlH_4$ and alkali and alkaline earth halides:

$$NaAlH_4 + LiCl \rightarrow LiAlH_4 + NaCl \tag{135}$$

$$2NaAlH_4 + MgCl_2 \rightarrow Mg(AlH_4)_2 + 2NaCl \tag{136}$$

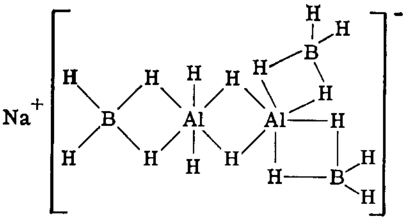
$$2NaAlH_4 + CaCl_2 \rightarrow Ca(AlH_4)_2 + 2NaCl \tag{137}$$

Lithium aluminum hydride, $Mg(AlH_4)_2$, and $Ca(AlH_4)_2$ were prepared by reaction of $NaAlH_4$ with the appropriate halide in tetrahydrofuran. If the resultant complex metal hydride was soluble in tetrahydrofuran, the product was separated from the NaCl by filtration; if not, it was separated from the NaCl by solvent extraction.

Wiberg and Schrauzer (*144*) reported the preparation of alane and borane adducts of $NaAlH_4$ by reaction of $NaAlH_4$ and aluminum hydride or diborane in tetrahydrofuran at low temperature. Addition of a tetrahydrofuran solution of $NaAlH_4$ to a solution of aluminum hydride in tetrahydrofuran at −40° resulted in the precipitation of $NaAlH_4 \cdot AlH_3 \cdot THF$ ($NaAl_2H_7 \cdot THF$). This white crystalline solid, although soluble in tetrahydrofuran at room temperature, was insoluble in diethyl ether and benzene. Evidence was presented to prove that the product was a true compound rather than a mixture of $NaAlH_4$ and $AlH_3$. The evidence was based on several factors. First, the Na/Al ratio of the product that precipitated from the reaction mixture at 40°, and also that precipitated from solution at room temperature on addition of diethyl ether was 1.0/2.0 in both cases. Second, if the product were a mixture of $NaAlH_4$ and $AlH_3$, it would have to contain 3 moles of tetrahydrofuran per molecule ($NaAlH_4 \cdot THF + AlH_3 \cdot 2THF = NaAlH_4, AlH_3, 3THF$) instead of one ($NaAl_2H_7 \cdot THF$). Third, the thermal stability of the product does not correspond to what would be expected for a mixture of $NaAlH_4$ and $AlH_3$. Wiberg reports that $AlH_3$ decomposes at 100°–140°, $NaAlH_4$ at 220°–240°, and $NaAl_2H_7$ at 130°–220°.

The formation of an alane adduct appears likely in light of the existence of similar adducts of $LiAlH_4$, i.e., $LiAl_2H_7$, and reported conductometric data. However, the proof presented is certainly not very rigorous. The thermal stability data do not seem to prove much since the stability of the proposed adduct is not much different than what might be expected for a physical mixture of $NaAlH_4$ and $AlH_3$. One can compare thermal stabilities only if the rates of heating during the stability studies are identical. Furthermore, the number of moles of solvent attached to the product depends on the method of drying. By subjecting $NaAlH_4 \cdot THF$ to vacuum (normal method for drying air-sensitive compounds), most of the solvated tetrahydrofuran can be removed. Under the same conditions over 50% of the tetrahydrofuran in $AlH_3 \cdot 2THF$ can be removed. With regard to the precipitation studies, if the product were a mixture of $NaAlH_4$ and $AlH_3$ in tetrahydrofuran solution, at −40° it is not unreasonable to expect almost all of both the $NaAlH_4$ and $AlH_3$ to precipitate. Likewise, if a solvent in which both $NaAlH_4$ and $AlH_3$ are insoluble (such as diethyl ether) is added in order to cause precipitation of the reaction mixture, it should not be considered unusual that both products would completely precipitate. The conductometric data presented by Wiberg and co-workers appear to be the most convincing evidence for the formation of $NaAl_2H_7$ in solution; however, little conclusion can be drawn from available information concerning the nature of the solid product.

Wiberg and co-workers reported the reaction of $NaAl_2H_7$ and diborane in tetrahydrofuran. The products $NaAl_2H_7 \cdot BH_3$, $NaAl_2H_7 \cdot 2BH_3$, and $NaAl_2H_7 \cdot 3BH_3$ were reported to possess unusual thermal stability (170°, 160°, and 190°, respectively). The reactions were run at −30° at which temperature the products precipitated and were isolated and analyzed. The only proof given to indicate that these products are single compounds and not mixtures of $NaBH_4$ and $AlH_3$ (or $AlH_3 \cdot nBH_3$) was based on the expected tetrahydrofuran content as a solvate, although $NaAl_2H_7 \cdot 2BH_3$ and $NaAl_2H_7 \cdot 3BH_3$ were isolated as tris-tetrahydrofuranate solvates. Although structures for these products were not suggested, it is difficult to see how a compound such as $NaAl_2H_7 \cdot nBH_3$ could be stable to 160°–190° when the molecules are held together by only single or double hydrogen bridge bonds. An attempt to represent $NaAl_2H_7 \cdot 3BH_3$ structurally shows a similarity to the type of bonding and structure known for $Al(BH_4)_3$. Aluminum borohydride releases diborane below 50°.



Wiberg also reported that the reaction of $NaAlH_4$ and diborane in tetrahydrofuran produced $NaAlH_4 \cdot nBH_3$ where $n = 1, 2, 3$, or 4. The compound $NaAlH_4 \cdot BH_3$ was reported to be stable to 400°. The only proof provided to distinguish the proposed product as a pure compound from a mixture was chemical analysis. Sodium and boron analyses exhibited the proper ratios; however, aluminum analyses were not provided. Sodium borohydride if formed in the reaction would precipitate from solution leaving $AlH_3$ in solution. Sodium borohydride decomposes at 400° under vacuum, which is the manner in which the stabilities of the proposed complexes were measured.

One of the most interesting reports in the complex metal hydride area over the past 15 years was made recently by Zakharkin and Gavrilenko (*153*). These workers reported the preparation of $Na_3AlH_6$ by the reaction of NaH and $NaAlH_4$ at 160° in heptane:

$$2NaH + NaAlH_4 \rightarrow Na_3AlH_6 \qquad (138)$$

Due to the insolubility of the product in all solvents tested, it could not be purified. Proof for the formation of $Na_3AlH_6$ was based on two observations: (1) extraction of the product with tetrahydrofuran did not result in the extraction of $NaAlH_4$, and (2) reaction of the product with diisobutylaluminum hydride resulted in the formation of $NaAlH_4$ and sodium diisobutylaluminum hydride, according to the following equation:

$$Na_3AlH_6 + 2(i\text{-}C_4H_9)_2AlH \rightarrow NaAlH_4 + 2NaAl(i\text{-}C_4H_9)_2H_2 \qquad (139)$$

The existence of $Na_3AlH_6$ and its method of preparation certainly appear reasonable. However, the proof submitted for the existence of this compound is hardly convincing. For example, if the NaH and $NaAlH_4$ did not react, would not this mixture react with $(i\text{-}C_4H_9)_2AlH$ just as if $NaAlH_4$ and NaH did react?

$$2NaH + NaAlH_4 + 2(i\text{-}C_4H_9)_2AlH \rightarrow NaAlH_4 + 2NaAl(i\text{-}C_4H_9)_2H_2 \qquad (140)$$

Also, since NaH and $NaAlH_4$ are both insoluble in hexane, it is not unreasonable that heating these two solids together at such a high temperature with stirring would result in NaH coating the surface of the $NaAlH_4$ particles. Furthermore, both the reactants and product are insoluble solids and therefore it seems unlikely that reaction would go to completion if it proceeds at all. It is highly possible that $Na_3AlH_6$ does exist and was prepared by this method; however, it certainly hasn't been proven. Comparison of powder diffraction patterns of $NaAlH_4$, NaH, Al, and the product of 2NaH + $NaAlH_4$ should provide the necessary information to establish the authenticity of the claim.

## V. Potassium Aluminum Hydride

### A. Properties and Structure

Very little is known about $KAlH_4$ since it has only recently been reported. The structure of $KAlH_4$ has not been determined; however, it is reasonable that it is an ionic compound consisting of $K^+$ and $(AlH_4)^-$ ions. It is insoluble in diethyl ether and benzene, but quite soluble in tetrahydrofuran and diglyme. Its increased thermal stability and decreased solubility compared to $LiAlH_4$ and $NaAlH_4$ are evidence of its increased ionic character as compared to the lighter metal complex aluminohydrides.

Dymova and co-workers (*29*) studied the thermal stability of $KAlH_4$ using a differential pyrometer. The results were interpreted as follows:

$$KAlH_4 \rightarrow KAlH_2 + H_2 \ (292°\text{–}315°) \tag{141}$$

$$KAlH_2 \rightarrow KH + Al + 1/2H_2 \ (335°\text{–}355°) \tag{142}$$

$$KH \rightarrow K + 1/2H_2 \ (425°\text{–}430°) \tag{143}$$

Two additional effects were observed: fusion of Al (664°–665°) and an unexplained transformation at 720°–730°.

### B. Preparations

The preparation of $KAlH_4$ was first reported by Ashby and co-workers (*2,7*) by direct synthesis from the elements:

$$K + Al + 2H_2 \rightarrow KAlH_4 \tag{144}$$

The desired product was isolated in 95% yield and 99% purity using toluene, diglyme, or tetrahydrofuran as a solvent. This reaction was best run in diglyme; however, temperatures lower than normally employed for the preparation of $LiAlH_4$ and $NaAlH_4$ were necessary due to solvent cleavage. Although $LiAlH_4$ and $NaAlH_4$ form stable etherates with diglyme, $KAlH_4$ was isolated as the ether-free product by toluene precipitation.

Clasen (*21*) and Zakharkin and Gavrilenko (*153*) have also reported the direct synthesis of $KAlH_4$ from the elements. Zakharkin used KH instead of potassium metal in hydrocarbon solvent operating in a rotating ball mill. Potassium aluminum hydride was isolated in 75% yield. Clasen reported the preparation of $KAlH_4$, but gave no experimental details or yield data.

Zakharkin and Gavrilenko reported the preparation of $KAlH_4$ by two additional methods. The first method (*151*) involved the reaction of KH and $AlCl_3$ in diethyl ether using triethylaluminum as a catalyst.The desired product was produced in 85% yield:

$$4KH + AlCl_3 \xrightarrow{Et_3Al} KAlH_4 + 3KCl \tag{145}$$

The second method consisted of the reaction of $LiAlH_4$ or $NaAlH_4$ and KH in diglyme solvent. The desired product was isolated in 85% yield:

$$LiAlH_4 + KH \rightarrow KAlH_4 + LiH \qquad (146)$$

The Russian workers also reported that $LiAlH_4$ could be prepared from $KAlH_4$ by a metathetical exchange reaction using LiCl:

$$KAlH_4 + LiCl \rightarrow LiAlH_4 + KCl \qquad (147)$$

## VI. Cesium Aluminum Hydride

The preparation of $CsAlH_4$ has only recently been reported by Ashby and co-workers (7). This complex metal hydride was prepared by reaction of cesium metal, aluminum powder, and hydrogen in toluene diluent using triethylaluminum as a catalyst at 130° and 4000 psi:

$$Cs + Al + 2H_2 \rightarrow CsAlH_4 \qquad (148)$$

Cesium aluminum hydride was isolated in 81% yield in a high state of purity. When diglyme was used as the solvent, poor results were obtained due to the cleavage of diglyme by cesium metal even at room temperature. Cesium aluminum hydride, however, does not cleave diglyme so that, after preparation in toluene, the reaction product was separated from excess aluminum powder by solution in diglyme. A white crystalline, high purity $CsAlH_4$ was precipitated from diglyme solution by the addition of toluene.

No other information concerning $CsAlH_4$ is available at this time.

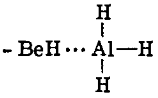
## VII. Beryllium Aluminum Hydride

Little is known about $Be(AlH_4)_2$. One of the problems in increasing the knowledge of beryllium-hydrogen compounds lies in the extreme toxicity of beryllium-containing compounds. Now that the toxicity factor has been realized, beryllium compounds are handled only with extreme caution. Not only are nitrogen dry-boxes used for transformations, but also all reactions and manipulations are carried out in large air flow capacity hoods.

Nothing is known about the structure of $Be(AlH_4)_2$. Although alkali metal aluminohydrides are considered to be highly ionic, this may not be the case with the alkaline earth complex aluminohydrides. Thus, the possibility of attachment of the $AlH_4$ group to an alkaline earth metal could be ionic (A), covalent via single hydrogen bridge bonds (B), or covalent via double hydrogen bridge bonds (C):

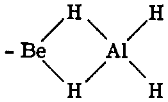
$-Be^{+}\ (AlH_4)^{-}$

(A)



$-BeH\cdots\overset{H}{\underset{H}{Al}}-H$

(B)



(C)

It would seem that the bonding in these compounds could be established through NMR studies.

Wiberg and Bauer (*119*) first reported the preparation of $Be(AlH_4)_2$ by reaction of $LiAlH_4$ and $BeCl_2$ in diethyl ether:

$$2LiAlH_4 + BeCl_2 \rightarrow Be(AlH_4)_2 + 2LiCl \tag{149}$$

The by-product LiCl was reported to precipitate from solution leaving the $Be(AlH_4)_2$ to be isolated from solution by solvent evaporation. Sometime later Wiberg reported (*148a*) that the above reaction could not be verified. Instead it was found that addition of $LiAlH_4$ to $BeCl_2$ or vice versa in diethyl ether resulted in the immediate precipitation of a white solid. The solid was found to be a mixture of $BeH_2$ and LiCl leaving the $AlH_3$ in solution:

$$2LiAlH_4 + BeCl_2 \rightarrow BeH_2 + 2LiCl + 2AlH_3 \tag{150}$$

The conclusion was drawn that $Be(AlH_4)_2$ may have been formed, but cannot exist in diethyl ether solution without dissociation.

$$Be(AlH_4)_2 \xrightarrow{Et_2O} BeH_2 + 2AlH_3 \tag{151}$$

Redistribution of $LiAlH_4$ and $Be(BH_4)_2$ in diethyl ether also resulted in the precipitation of $BeH_2$:

$$2LiAlH_4 + Be(BH_4)_2 \rightarrow BeH_2 + 2AlH_3 + 2LiBH_4 \tag{152}$$

Wiberg and Bauer reported the preparation of $Be(AlH_4)_2$ by the reaction of $NaAlH_4$ and $BeCl_2$ in tetrahydrofuran; however, this method did not produce a pure product. The reaction of $BeH_2$ and $AlH_3$ in tetrahydrofuran was reported to produce $Be(AlH_4)_2$ in a pure state as the tris-tetrahydrofuranate:

$$BeH_2 + 2AlH_3 \xrightarrow{THF} Be(AlH_4)_2 \cdot 3THF \tag{153}$$

The $BeH_2$ was prepared by the reaction of $LiAlH_4$ and $BeCl_2$ in diethyl ether, Eq. (150). Beryllium hydride was not initially soluble in tetrahydrofuran; however, over a period of 3 days all of the compound dissolved. The product was isolated by evaporation of the tetrahydrofuran solvent. Elemental analysis of the product showed Be, Al, and H present in the ratio of 1.0:2.0:8.1. A thermal stability study of the product indicated mostly tetrahydrofuran liberation up to 83°. At 136° the product turned light gray and at 145° dark gray. In tetrahydrofuran the product was determined to be monomeric, based on $Be(AlH_4)_2$ as the product. The molecular weight report appears important since at no point was it established that the product was not a mixture of $BeH_2$ and $AlH_3$. The long period of time necessary for $BeH_2$ to solubilize is consistent with the polymeric nature of

$BeH_2$ and does not necessarily imply reaction with the aluminum hydride. When diethyl ether was added to the tetrahydrofuran solution (produced on addition of $BeH_2$ and $AlH_3$), $BeH_2$ as a white solid precipitated. Under the same conditions a solution of $AlH_3$ was reported to remain clear.

Wood and Brenner (*150*) claimed to have prepared $Be(AlH_4)_2$ in diethyl ether by the method reported by Wiberg and Bauer. After precipitation of LiCl and some $Be(AlH_4)_2$, the resulting solution had a Be:Al:H ratio of 1:1.83:9.2. The solution was stable for several days at $-10°$ to $+10°$; however, it decomposed in several hours at the boiling point of diethyl ether. These workers made no serious attempt to establish the nature of the product of this reaction since they were interested only in repeating the method reported by Wiberg in order to prepare $Be(AlH_4)_2$ for beryllium electrodeposition studies.

## VIII. Magnesium Aluminum Hydride

Little is known about $Mg(AlH_4)_2$. The first report of its preparation was made by Wiberg and Bauer in 1950 (*118*). They reported that reaction of $MgBr_2$ and $LiAlH_4$ in diethyl ether solution produced $Mg(AlH_4)_2$; however, few experimental details were given:

$$2LiAlH_4 + MgBr_2 \rightarrow Mg(AlH_4)_2 + 2LiBr \tag{154}$$

The LiBr was reported to be relatively insoluble compared to the $Mg(AlH_4)_2$, the desired product being isolated by removal of the diethyl ether solvent under vacuum.

Other reports by Wiberg and Bauer provided additional methods for the preparation of $Mg(AlH_4)_2$. Magnesium hydride was reported to react with $AlCl_3$ in diethyl ether (*118, 121*) or with $AlH_3$ (*116, 122*) to produce $Mg(AlH_4)_2$:

$$4MgH_2 + 2AlCl_3 \rightarrow Mg(AlH_4)_2 + 2MgCl_2 \tag{155}$$

$$MgH_2 + 2AlH_3 \rightarrow Mg(AlH_4)_2 \tag{156}$$

The $Mg(AlH_4)_2$ produced in the above reactions was reported to be soluble in diethyl ether and stable to 140°. The decomposition of $Mg(AlH_4)_2$ was reported to proceed according to the equation:

$$Mg(AlH_4)_2 \rightarrow MgH_2 + 2Al + 3H_2 \tag{157}$$

Sometime later (1959) Wiberg (*148a*) reported that the preparation of $Mg(AlH_4)_2$ from $LiAlH_4$ and $MgBr_2$ in diethyl ether could not be substantiated. However, when the reaction was run in tetrahydrofuran, $BrMgAlH_4$ precipitated from solution. Further reaction with excess $LiAlH_4$ did not result in the formation of $Mg(AlH_4)_2$. Complete conversion of $BrMgAlH_4$ to $Mg(AlH_4)_2$ was accomplished only by reaction with $NaAlH_4$; however, no experimental details were given. Whether or not the product of this reaction has the same physical properties as originally reported for $Mg(AlH_4)_2$, prepared by the reaction of $LiAlH_4$ and $MgBr_2$ or the other process involving $MgH_2$, is not known. In the absence of more information it would appear that more work is needed to define the physical properties and method of preparation of $Mg(AlH_4)_2$.

Two German patents have issued describing the preparation of $Mg(AlH_4)_2$. The first patent (*54a*) describes a process whereby a Grignard reagent is hydrogenated in diethyl ether solution and the resulting white solid used to reduce an aluminum halide. Three reactions were proposed to represent the formation of the products:

$$4RMgX + AlX_3 + 4H_2 \rightarrow XMgAlH_4 + 3MgX_2 + 4RH \quad (158)$$

$$3RMgX + AlX_3 + 3H_2 \rightarrow AlH_3 + 3MgX_2 + 3RH \quad (159)$$

$$2XMgAlH_4 \rightarrow Mg(AlH_4)_2 + MgX_2 \quad (160)$$

Few details concerning the separation, isolation, and identification of the products were given. It had been previously reported that hydrogenolysis of Grignard compounds at 150° produced a mixture of $MgH_2$ and $MgX_2$ (*118*). This has been substantiated by Becker and Ashby (*13*). Supposedly then the products arise through reduction of $AlCl_3$ by $MgH_2$. This would account for the formation of $AlH_3$ and $Mg(AlH_4)_2$. Chloromagnesium aluminohydride could arise by redistribution of $MgCl_2$ and $Mg(AlH_4)_2$. Redistribution of $MgCl_2$ and $Mg(BH_4)_2$ to $ClMgBH_4$ has been recently reported by Becker and Ashby (*14*).

The second German patent (*32a*) reported the preparation of $AlH_3$ or $Mg(AlH_4)_2$ by the reaction of $MgH_2$, Al powder, and $AlCl_3$ in diethyl ether solution. Few experimental details were given and $Mg(AlH_4)_2$ was not characterized.

Clasen (*21*) reported that $Mg(AlH_4)_2$ was prepared by reaction of $MgH_2$, Al, and $H_2$; however, no experimental details were given. The properties given for $Mg(AlH_4)_2$ were exactly the same as those reported by Wiberg and Bauer (*118*) for $Mg(AlH_4)_2$ prepared from $LiAlH_4$ and $MgBr_2$, a report which was later retracted. Robinson (*31*) reported the preparation of $Mg(AlH_4)_2$ by reaction of $NaAlH_4$ and $MgCl_2$ in diethyl ether or tertiary amine solvent; however, no properties of the product were reported:

$$2NaAlH_4 + MgCl_2 \rightarrow Mg(AlH_4)_2 + 2NaCl \quad (161)$$

It appears that there is some confusion in the literature concerning the properties of $Mg(AlH_4)_2$ and even some question concerning the authenticity of its reported existence. The first report concerning $Mg(AlH_4)_2$ described the properties of this compound in detail. Several subsequent preparations reported exactly the same physical properties. Since the original report concerning $Mg(AlH_4)_2$ has been retracted by Wiberg, the situation in this area has become somewhat clouded.

## IX. Calcium Aluminum Hydride

The first reported preparation of $Ca(AlH_4)_2$ was made by Finholt (*36*) in 1951. The report was concerned with the preparation of diborane from $Ca(AlH_4)_2$ and boron trifluoride; however, the preparation of $Ca(AlH_4)_2$ from $CaH_2$ and $AlCl_3$ was also described:

$$3Ca(AlH_4)_2 + 8BF_3 \rightarrow 3CaF_2 + 6AlF_3 + 4B_2H_6 \tag{162}$$

$$4CaH_2 + 2AlCl_3 \rightarrow Ca(AlH_4)_2 + 3CaCl_2 \tag{163}$$

The reaction was carried out in tetrahydrofuran and the product was isolated from solution as the bis-tetrahydrofuranate. Later, Schwab and Wintersberger (*96*), realizing the sparsity of information concerning this compound, investigated its preparation and physical properties more thoroughly. They prepared $Ca(AlH_4)_2$ by reaction of finely divided $CaH_2$ (suspended in tetrahydrofuran) and $AlCl_3$ at reflux temperature. The presence of a trace of iodine improved the yield. The solvent was removed without decomposition of the product, which was found to be very soluble in tetrahydrofuran but insoluble in diethyl ether, dioxane, and benzene. These workers found that the reaction of $CaH_2$ and $AlCl_3$ could be controlled to produce either $Ca(AlH_4)_2$ or $AlH_3$:

$$3CaH_2 + 2AlCl_3 \rightarrow 3CaCl_2 + 2AlH_3 \tag{164}$$

They also found that $AlH_3$ could be produced in 85% yield by reaction of $Ca(AlH_4)_2$ and $AlCl_3$ in tetrahydrofuran:

$$3Ca(AlH_4)_2 + 2AlCl_3 \rightarrow 8AlH_3 + 3CaCl_2 \tag{165}$$

In 1956 Finholt and co-workers (*37*, *43*) described a two-step process for preparing $Ca(AlH_4)_2$ similar to the two-step process for $NaAlH_4$ previously described (Section IV,B) by the same workers. The process involves the following two steps:

$$3Ca(AlH_4)_2 + 2AlCl_3 \rightarrow 8AlH_3 + CaCl_2 \tag{166}$$

$$8AlH_3 + 4CaH_2 \rightarrow 4Ca(AlH_4)_2 \tag{167}$$

The process requires the initial preparation of $AlH_3$ from $LiAlH_4$ and $AlCl_3$ and also requires the recycle of the major portion of the $Ca(AlH_4)_2$ formed. The advantage of this process over the one-step reaction involving $CaH_2$ and $AlCl_3$ reportedly is due to the ease of reaction and high yields experienced in the two-step process. A process improvement patent describing the preparation of $Ca(AlH_4)_2$ from $CaH_2$ and $AlCl_3$ in tetrahydrofuran was published by Conn and Taylor (*22*). Yields of 70–80% were reported in tetrahydrofuran-diglyme solvent using $I_2$ as a catalyst.

Calcium aluminum hydride was also prepared by the reaction of $CaH_2$ and trimethylamine-alane, according to a report by Ruff and Hawthorne (*89*):

$$CaH_2 + 2AlH_3{\cdot}N(CH_3)_3 \rightarrow Ca(AlH_4)_2 + N(CH_3)_3 \tag{168}$$

This reaction is similar to the preparations previously described by the same authors for $LiAlH_4$ and $NaAlH_4$ involving the reaction of the appropriate metal hydride with $AlH_3{\cdot}N(CH_3)_3$.

Clasen (*21*) reported the preparation of $Ca(AlH_4)_2$ from $CaH_2$, Al, and $H_2$; however, no experimental details were given:

$$CaH_2 + 2Al + 3H_2 \rightarrow Ca(AlH_4)_2 \tag{169}$$

Robinson (*31*) described the preparation of $Ca(AlH_4)_2$ by the metathetical reaction involving $NaAlH_4$ and $CaCl_2$; the properties of $Ca(AlH_4)_2$ were not reported:

$$2NaAlH_4 + CaCl_2 \rightarrow Ca(AlH_4)_2 + 2NaCl \tag{170}$$

Wiberg and co-workers (*148a*) reported, from conductometric titration data, adduct formation between $Ca(AlH_4)_2$ and $AlH_3$:

$$Ca(AlH_4)_2 + 2AlH_3 \rightarrow Ca(AlH_4)_2{\cdot}2AlH_3 \tag{171}$$

The formation of $Ca(Al_2H_7)_2$ was based solely on the conductometric titration data. The compound was not isolated and therefore its properties were not determined.

Conductometric titrations were also reported by Wiberg and co-workers to establish the existence of borane adducts of $Ca(AlH_4)_2$. When diborane was passed into a tetrahydrofuran solution of $Ca(AlH_4)_2$, borane adducts similar to the type previously described for $NaAlH_4$ were reported:

$$Ca(AlH_4)_2 + nBH_3 \rightarrow Ca(AlH_4{\cdot}nBH_3)_2 \tag{172}$$

where $n = 1, 2, 3$, or 4. The reaction products were isolated by removing the solvent under vacuum. The thermal stability of the four adducts was investigated; however, no definite conclusions concerning the stability of the compounds were drawn. The decomposition of the adducts was believed to proceed through $Ca(BH_4)_2$:

$$Ca(AlH_4{\cdot}BH_3)_2 \rightarrow Ca(BH_4)_2 + 2Al + 3H_2 \tag{173}$$

Two patents describe uses of $Ca(AlH_4)_2$ as a reducing agent. The reduction of $SiCl_4$ to $SiH_4$ was reported (*15*) as a route to high purity Si for transistors, and the reduction of $AlCl_3$ to $AlH_3$ was reported as a good route to $AlH_3$ in tetrahydrofuran solution (*54*).

## X. Analysis of Complex Aluminohydrides

The standard method of analysis of complex aluminohydrides involves hydrolysis of the hydride followed by quantitative measurement of the hydrogen evolved. Due to the violent nature of the reaction of a complex aluminohydride with water, the hydride should be diluted with some liquid of low vapor pressure such as diglyme and the water added as a dilute solution in diglyme. The evolution of $H_2$ is quantitative and Al:H ratios for $LiAlH_4$ and $NaAlH_4$ of 1.0:4.0 can be achieved, although the hydrogen value normally runs about 2–3% low. A similar technique, in which the increase in pressure after hydrolysis is measured directly, also has been found to be successful (*66*).

Complex aluminohydrides can also be analyzed by volumetric techniques. For example, $LiAlH_4$ can be quickly and conveniently analyzed by addition of excess standard iodine in benzene followed by back titration of the excess iodine with sodium thiosulfate (*35*).

For analyzing standard solutions of $LiAlH_4$ in diethyl ether or $NaAlH_4$ in tetrahydrofuran, one need determine only the aluminum concentration by EDTA titration. Experience has shown that $H_2$ evolution analysis always gives an Al:H ratio of about 1.0:3.9; therefore, aluminum analysis by some simple titrimetric method such as EDTA provides a quick and simple method of determining the concentration of a standard solution.

## XI. Summary

Complex metal hydrides in general are white crystalline solids, stable to dry air, soluble in certain ether-type solvents, very sensitive to moisture in the air or any protic compounds, and are very reactive as reducing agents toward both organic and inorganic compounds. Most complex metal hydrides have been prepared by the reaction of a metal halide with $LiAlH_4$:

$$n\mathrm{LiAlH_4} + \mathrm{MX}_n \rightarrow \mathrm{M(AlH_4)}_n + n\mathrm{LiX} \qquad (174)$$

Complex metal hydrides react with metal-halogen, metal-alkoxy, and metal-alkyl compounds to form the corresponding metal hydride and with any active hydrogen compound to rapidly release hydrogen.

Major contributions by Wiberg, Zakharkin, Finholt, and Brown are discussed in some detail. Important contributions needing more study are pointed out in an effort to warn the reader of weakly established principles in this area of chemistry.

Some physical and thermodynamic properties of the known complex aluminohydrides are provided in Tables III, IV, and V (*25a*, *100*).

TABLE III

PHYSICAL PROPERTIES OF COMPLEX METAL HYDRIDES

| | Solubility[a] (25°) (gm/100 gm solvent) | | | | |
|---|---|---|---|---|---|
| Hydride | $Et_2O$ | THF | DMC | Thermal stability (°C) | Density (gm/cc) |
| $LiAlH_4$ | 30 | 13 | 10 | 120 | 0.917 |
| $NaAlH_4$ | insol | 20 | 15 | 183 | 1.28 |
| $KAlH_4$ | insol | ss | s | >200 | 1.33 |
| $CsAlH_4$ | insol | insol | s | — | 2.84 |
| $Be(AlH_4)_2$ | dec | s | — | — | — |
| $Mg(AlH_4)_2$ | s(?) | — | — | 140(?) | — |
| $Ca(AlH_4)_2$ | — | s | — | — | — |

[a] s = soluble, ss = slightly soluble, insol = insoluble, dec = decomposes.

TABLE IV

HEATS AND FREE ENERGIES AT 25° OF DECOMPOSITION REACTIONS OF THE TYPE:[a] $XMH_4 \rightarrow XH(C) + M(C) + 3/2H_2(g)$

| Hydride | $H^0$ (kcal/mole) | $F^0$ (kcal/mole) |
|---|---|---|
| $LiAlH_4$ | +6.8 | −3.9 |
| $NaAlH_4$ | +13.5 | +3.0 |
| $KAlH_4$ | +26.0 | +14.9 |
| $CsAlH_4$ | +27.5 | +16.5 |

[a] Reference *(100)*.

TABLE V

HEATS AND FREE ENERGIES OF FORMATION AT 25° IN KCAL/MOLE

| Hydride | $-H_f$ | $-F_f^0$ | $-298.15S_f^0$ | $S^0$ |
|---|---|---|---|---|
| $LiAlH_4$ | 28.4 | 12.9 | 15.6 | 23.5 |
| $NaAlH_4$ | 27.0 | 11.6 | 15.4 | 29.6 |
| $KAlH_4$ | 39.8 | 23.8 | 16.0 | 30.8 |
| $CsAlH_4$ | 39.4 | 23.5 | 15.9 | 36.0 |

## REFERENCES

1. Anderson, A. W., Bruce, J. M., Merckling, N. G., and Truett, W. L., U. S. Patent 2,905,645 (1959).
2. Ashby, E. C., French Patent 1,235,689 (1960).
3. Ashby, E. C., *Chem. Ind. (London)* p. 208 (1962).
4. Ashby, E. C., *J. Am. Chem. Soc.* **86,** 1882 (1964).
5. Ashby, E. C., *Advan. Organomet. Chem.* **3,** 371 (1965).

*6.* Ashby, E. C., and Prather, J., *J. Am. Chem. Soc.* **88,** in press (1966).

*7.* Ashby, E. C., Brendel, G. J., and Redman, H. E., *Inorg. Chem.* **2,** 499 (1963).

*8.* Baker, B. B., Jr., and MacNevin, W. M., *Anal. Chem.* **22,** 364 (1950).

*9.* Banus, M. D., U. S. Patent 3,112,989 (1963).

*10.* Banus, M. D., U. S. Patent 3,134,417 (1964).

*11.* Barbaras, G., Barbaras, G. D., Finholt, A. E., and Schlesinger, H. I., *J. Am. Chem. Soc.* **70,** 877 (1948).

*12.* Barbaras, G. D., Dillard, C., Finholt, A. E., Wartik, T., Wilzbach, K. E., and Schlesinger, H. I., *J. Am. Chem. Soc.* **73,** 4585 (1951).

*12a.* Barton, D. H. R., and Rosenfelder, W. J., *J. Chem. Soc.* p. 2381 (1951).

*13.* Becker, W. E., and Ashby, E. C., *J. Org. Chem.* **29,** 954 (1964).

*14.* Becker, W. E., and Ashby, E. C., *Inorg. Chem.* **4,** 1816 (1965).

*15.* Bell Telephone Manufacturing Co., Belgian Patent 561,160 (1958).

*16.* Biggs, M. W., Kritchevsky, D., and Kirk, M. R., *Anal. Chem.* **24,** 223 (1952).

*17.* Bragdon, R. W., U. S. Patent 2,680,059 (1953).

*18.* Brown, H. C., and Shoaf, C. J., *J. Am. Chem. Soc.* **86,** 1079 (1964).

*19.* Brown, H. C., Stehle, P. F., and Tierney, P. A., *J. Am. Chem. Soc.* **79,** 2020 (1957).

*20.* Chattoraji, S. C., Hollingsworth, C. A., McDaniel, D. H., and Smith, G. B., *J. Inorg. Nucl. Chem.* **24,** 101 (1962).

*21.* Clasen, H., *Angew. Chem.* **73,** 322 (1961).

*21a.* Coates, G. E., *J. Chem. Soc.* p. 3481 (1950).

*22.* Conn, D. B., and Taylor, R. C., U. S. Patent 2,999,005 (1958).

*23.* Coover, H. W., Jr., and Joyner, F. B., U. S. Patent 2,967,856 (1961).

*24.* Coover, H. W., Jr., and Joyner, F. B., U. S. Patent 3,026,311 (1962).

*25.* Davidson, J. M., and Wartik, T., *J. Am. Chem. Soc.* **82,** 5506 (1960).

*25a.* Davis, W. D., Mason, L. S., and Stegeman, G., *J. Am. Chem. Soc.* **71,** 2775 (1949).

*26.* E. I. du Pont de Nemours & Co., British Patent 783,487 (1957).

*27.* E. I. du Pont de Nemours & Co., British Patent 819,279 (1959).

*28.* Dymova, T. N., Eliseeva, N. G., and Selivokhina, M. S., *Dokl. Akad. Nauk SSSR* **148,** 589 (1963).

*29.* Dymova, T. N., Selivokhina, M. S., and Eliseeva, N. G., *Dokl. Akad. Nauk SSSR* **153,** 133 (1963).

*30.* English, W. D., Taurins, A., and Nicholls, R. V., *Can. J. Chem.* **30,** 646 (1952).

*31.* Ethyl Corp., British Patent 905,985 (1962).

*32.* Evans, G. G., Kennedy, J. K., and Del Greco, F. P., *J. Inorg. Nuclear Chem.* **4,** 40 (1957).

*32a.* Farbenfabriken Bayer A.-G., British Patent 785,348 (1957).

*33.* Fasolino, L. G., *NASA* (*Natl. Aeron. Space Admin.*) *Doc.* **N63-15746,** 28 (1963).

*34.* Fasolino, L. G., *J. Chem. Eng. Data* **9,** 68 (1964).

*35.* Felkin, H., *Bull. Soc. Chim. France* [5] **18,** 347 (1951).

*36.* Finholt, A. E., U. S. Patent 2,550,985 (1951).

*37.* Finholt, A. E., British Patent 760,774 (1956).

*38.* Finholt, A. E., U. S. Patent 2,940,935 (1960).

*39.* Finholt, A. E., and Jacobson, E. C., *J. Am. Chem. Soc.* **74,** 3943 (1952).

*40.* Finholt, A. E., Bond, A. C., Wilzbach, K. E., and Schlesinger, H. I. *J. Am. Chem. Soc.* **69,** 2692 (1947).

*41.* Finholt, A. E., Bond, A. C., and Schlesinger, H. I., *J. Am. Chem. Soc.* **69,** 1199 (1947).

*42.* Finholt, A. E., Jacobson, E. C., Ogard, A. E., and Thompson, P., *J. Am. Chem. Soc.* **77,** 4163 (1955).

*43.* Finholt, A. E., Barbaras, G. D., Barbaras, G. K., Vrry, G., Wartik, T., and Schlesinger, H. I., *J. Inorg. Nucl. Chem.* **1,** 317 (1955).

*44.* Finholt, A. E., Helbing, C., Swhof, V., Nielson, L., and Jacobson, E., *Inorg. Chem.* **2,** 504 (1963).

*45.* Freedman, L. D., and Doak, G. O., *J. Am. Chem. Soc.* **74,** 3414 (1952).

*46.* Fulton, G., British Patent 757,524 (1956).

*47.* Garner, W. E., and Haycock, E. W., *Proc. Roy. Soc.* **A211,** 335 (1952).

*48.* Gaylord, N. G., and Mark, H. T., *Advan. Chem. Ser.* **34,** 127 (1962).

*49.* Gilman, H., and Branner, C. G., *J. Am. Chem. Soc.* **73,** 4640 (1951).

*50.* Ginsberg, A. P., Miller, D. M., and Koubek, E., *J. Am. Chem. Soc.* **83,** 4909 (1961).

*51.* Good, C. D., and Batha, H. D., U. S. Patent 2,867,499 (1959).

*52.* Guild, L. V., Hollingsworth, C. A., McDaniel, D. H., and Poddar, S. K., *Inorg. Chem.* **1,** 921 (1962).

*53.* Hans Heinrich Hütte, British Patent 707,851 (1954).

*53a.* Haubenstock, H., and Eliel E. I., *J. Am. Chem. Soc.* **84,** 2363 (1962).

*54.* Hertwig, A., German Patent 911,131 (1954).

*54a.* Hertwig, A., German Patent 921,986 (1955).

*55.* Harris, P. M., and Meibohm, E. P., *J. Am. Chem. Soc.* **69,** 1231 (1947).

*56.* Hawthorne, M. F., *Chem. Ind.* (*London*) p. 1243 (1957).

*57.* Hinckley, A. A., and Del-Guidise, F. P., U. S. Patent 2,900,224 (1959).

*58.* Hoffmann, A. N., and Spurlin, H. M., French Patent 1,273,454 (1961).

*59.* Hoffmann-LaRoche and Co., British Patent 888,045 (1952).

*60.* Hollingsworth, C. A., Smalley, E. W., and Podder, S. N., *Inorg. Chem.* **3,** 222 (1964).

*61.* Harvot, R. J., and Furst, A., *J. Am. Chem. Soc.* **74,** 562 (1952).

*62.* Huber, L. L., and Grosse, A. V., TID-12798 Fourth Annual Progress Report, Part I (1960–1961).

*63.* Johnson, O. H., and Harris, D. M., *J. Am. Chem. Soc.* **72,** 5564 (1950).

*64.* Klanberg, F., and Kohlschutter, H. W., *Chem. Ber.* **94,** 781 (1961).

*65.* Kollonitsch, J., *Nature* **189,** 1005 (1961).

*66.* Krynitsky, J. A., Johnson, J. E., and Carhart, H. W., *Anal. Chem.* **20,** 311 (1948).

*67.* Krynitsky, J. A., Johnson, J. E., and Carhart, H. W., *J. Am. Chem. Soc.* **70,** 486 (1948).

*68.* Lippincott, E. R., *J. Chem. Phys.* **17,** 1351 (1949).

*69.* Lord, R. C., and Nielsen, R., *J. Chem. Phys.* **19,** 1 (1951).

*70.* Macklen, E. D., *J. Chem. Soc.* p. 1984 (1959).

*71.* Mahe, J., Rollet, J., and Willemart, A., *Bull. Soc. Chim. France* [5] **16,** Part 1, 481 (1949).

*71a.* Mason, R. W., and Kelley, D. H., U. S. Patent 3,043,664 (1962).

*71b.* Matsuura, T., *Kagaku No Ryoiki* (*J. Japan. Chem.*) **7,** 733 (1953).

*72.* Maybury, P. C., and Koski, W. S., *J. Chem. Phys.* **21,** 742 (1953).

*72a.* Metallgesellschaft, British Patent 840,572 (1958).

*73.* Mikheeva, V. I., Fedneva, E. M., and Shnitkova, F. L., *Zh. Neorgan. Khim.* **1,** 2440 (1952).

*74.* Mikheeva, V. I., Seeivokhina, M. S., and Leonova, V. V., *Zh. Neorgan. Khim.* **4,** 2705 (1959).

75. Mikheeva, V. I., Seeivokhina, M. S., and Krykova, A., *Dokl. Akad. Nauk SSSR* **145,** 793 (1962).
76. Mirza, R., *Nature* **170,** 669 (1952).
77. Moffett, R. B., and Aspergren, B. D., *Chem. Eng. News* **32,** 4328 (1954).
78. Mulley, R. D., and Small, P. A., *British Patent* 827,229 (1960).
79. Nöth, H., *Angew. Chem.* **73,** 371 (1961).
80. Nöth, H., British Patent 820,513 (1959).
81. Nowlin, G., and Lyons, H. D., U. S. Patent 2,944,048 (1960).
82. Phillips Petroleum Co., British Patent 848,064 (1960).
83. Phillips Petroleum Co., British Patent 848,067 (1960).
84. Phillips Petroleum Co., British Patent 852,277 (1960).
84a. Paddock, N. L., *Nature* **167,** 1070 (1951).
85. Powers, J. C., U. S. Patent 3,119,651 (1964).
86. Raum, A. L., British Patent 827,462 (1960).
86a. Roman, P., and Mozes, G., *Rev. Chim.* (*Bucharest*) **11,** 464 (1960).
87. Rosenmund, P., and Matti, J., *Chem. Ber.* **85,** 152 (1952).
87a. Ruff, J. K., *Inorg. Chem.* **2,** 515 (1963).
88. Ruff, J. K., and Hawthorne, M. F., *J. Am. Chem. Soc.* **82,** 2141 (1960).
89. Ruff, J. K., and Hawthorne, M. F., *J. Am. Chem. Soc.* **83,** 535 (1961).
90. Safety, *Chem. Eng. News* **39,** 40 (1961).
91. Schaeffer, G. W., Roscoe, J. S., and Stewart, A. C., *J. Am. Chem. Soc.* **78,** 729 (1956).
92. Schlesinger, H. I., and Finholt, A. E., U. S. Patent 2,576,311 (1951).
93. Schlesinger, H. I., and Finholt, A. E., U. S. Patent 2,567,972 (1951).
94. Schultz, O. E., and Schnekenburger, J. S., German Patent 1,086,217 (1957).
95. Schultz, P. E., and Schnekenburger, J. S., German Patent 1,084,700 (1960).
96. Schwab, W., and Wintersberger, K., *Z. Naturforsch.* **8b,** 690 (1953).
97. Seidl, V., *Sb. Vysoke Chem.-Technol. v Praze, Oddil Fak. Anorg. Org. Technol.* **5,** (1958).
98. Semenenko, K. N., Turova, N. Y., and Urayboeva, R. N., *Zh. Neorgan. Khim.* **5,** 508 (1960).
99. Shapiro, I., Weiss, H. G., Skolnik, S., and Smith, G. B., *J. Am. Chem. Soc.* **74,** 901 (1952).
100. Smith, M. B., and Bass, G. E., *J. Chem. Eng. Data* **8** (3), 342 (1963).
100a. Stewart, A. C., and Schaeffer, G. W., *J. Inorg. Nucl. Chem.* **3,** 194 (1956).
101. Sujishi, S., and Keith, J. N., *J. Am. Chem. Soc.* **80,** 4138 (1958).
102. Szarvasi, E., French Patent 1,212,846 (1960).
103. Szarvasi, E., French Patent 1,320,642 (1960).
104. Szarvasi, E., French Patent 1,233,557 (1960).
105. Szarvasi, E., French addn. 74,678 (1961).
105a. Topchiev, A. V., Tolchinsku, I. M., and Krentsel, B. A., *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* p. 375 (1958).
105b. Van Artsdalen, E. R., and Gavis, J., *J. Am. Chem. Soc.* **74,** 3196 (1952).
106. van Langen, J. O. M., and Plas, T. V. D., *Rese. Correspondence,* Suppl. to *Research* (*London*) **1** (2) (1954).
107. Vit, J., Petra, F., Landa, S., Bartoviky, T., Hehner, P., Mosteskj, J., and Prochayka, V., Czechoslovakian Patent 89,103 (1959).
108. Vit, J., Prochayka, V., and Petra, F., *Chem. Prumysl* **10,** 183 (1960).
109. Warf, J. C., and Feitknecht, W., *Helv. Chim. Acta* **33,** 613 (1950).

*110.* West, R., *J. Am. Chem. Soc.* **74,** 4363 (1952).
*111.* Weil, T., Prys, B., and Erlenmeyer, H., *Helv. Chim. Acta* **35,** 616 (1952).
*112.* Weinmayr, V., U. S. Patent 2,975,159 (1961).
*113.* Wender, I., Friedel, R. A., and Orchin, M., *J. Am. Chem. Soc.* **71,** 1140 (1949).
*114.* Wiberg, E., *Z. Naturforsch.* **6b,** 393 (1951).
*115.* Wiberg, E., German Patent 893,339 (1953).
*116.* Wiberg, E., *Angew. Chem.* **65,** 16 (1953).
*117.* Wiberg, E., *European Sci. Notes* No. 7–15, 174 (1953).
*118.* Wiberg, E., and Bauer, R., *Z. Naturforsch.* **5b,** 394 (1950).
*119.* Wiberg, E., and Bauer, R., *Z. Naturforsch* **6b,** 171 (1951).
*120.* Wiberg, E., and Bauer, R., *Z. Naturforsch.* **6b,** 392 (1951).
*121.* Wiberg, E., and Bauer, R., *Z. Naturforsch.* **7b,** 131 (1952).
*122.* Wiberg, E., and Bauer, R., *Chem. Ber.* **85,** 593 (1952).
*122a.* Wiberg, E., and Gosele, W., *Z. Naturforsch.* **11b,** 485 (1956).
*123.* Wiberg, E., and Graf, H., Diploma work of H. Graf, Munich, 1953.
*124.* Wiberg, E., and Henle, W., *Z. Naturforsch.* **6b,** 461 (1951).
*125.* Wiberg, E., and Henle, W., *Z. Naturforsch.* **7b,** 250 (1952).
*126.* Wiberg, E., and Lacal, R. V., *Rev. Acad. Cienc. Exact. Fis.-Quim. Nat. Zaragoza* **6**(2), 25 (1951).
*126a.* Wiberg, E., and Lacal, R. V., *Rev. Acad. Cienc. Exact. Fis. nat.* **10**(1), 97 (1955).
*127.* Wiberg, E., and Modritzer, K., *Z. Naturforsch.* **11b,** 747 (1956).
*128.* Wiberg, E., and Modritzer, K., *Z. Naturforsch.* **11b,** 748 (1956).
*129.* Wiberg, E., and Modritzer, K., *Z. Naturforsch.* **11b,** 750 (1956).
*130.* Wiberg, E., and Modritzer, K., *Z. Naturforsch.* **11b,** 751 (1956).
*131.* Wiberg, E., and Modritzer, K., *Z. Naturforsch.* **11b,** 753 (1956).
*132.* Wiberg, E., and Modritzer, K., *Z. Naturforsch.* **11b,** 755 (1956).
*133.* Wiberg, E., and Modritzer, K., *Z. Naturforsch.* **12b,** 123 (1957).
*134.* Wiberg, E., and Muller-Schiedmayer, G., *Chem. Ber.* **92,** 2372 (1959).
*135.* Wiberg, E., and Muller-Schedmayer, G., *Z. Anorg. Allgem. Chem.* **308,** 352 (1961)
*136.* Wiberg, E., and Neumeier, U., German Patent 1,080,527 (1960).
*137.* Wiberg, E., and Neumeier, U., British Patent 863,491 (1961).
*138.* Wiberg, E., and Schmidt, M., *Z. Naturforsch.* **6b,** 172 (1951).
*138a.* Wiberg, E., and Schmidt, M., *Z. Naturforsch.* **6b,** 333 (1951).
*139.* Wiberg, E., and Schmidt, M., *Z. Naturforsch.* **6b,** 460 (1951).
*140.* Wiberg, E., and Schmidt, M., *Z. Naturforsch.* **7b,** 59 (1952).
*141.* Wiberg, E., and Schmidt, M., German Patent 893,789 (1953).
*142.* Wiberg, E., and Schmidt, M., German Patent 931,527 (1955).
*143.* Wiberg, E., and Schmidt, M., German Patent 937,823 (1956).
*144.* Wiberg, E., and Schrauzer, G. N., Diploma work of G. N. Schrauzer, Munich, 1956.
*145.* Wiberg, E., and Schrauzer, G. N., German Patent 1,066,553 (1960).
*146.* Wiberg, E., and Uson, R., *Z. Naturforsch.* **6b,** 392 (1951).
*147.* Wiberg, E., Henle, W., and Bauer, R., *Z. Naturforsch.* **6b,** 393 (1951).
*148.* Wiberg, E., Bauer, R., Schmidt, M., and Uson, R., *Z. Naturforsch.* **6b,** 393 (1951).
*148a.* Wiberg, E., and students, The reactions of hydrides and double hydride. Institute for Inorganic Chemistry, Munich, 1959.
*149.* Wittig, G., and Bille, H., *Z. Naturforsch.* **6b,** 226 (1951).
*150.* Wood, G. B., and Brenner, A., *J. Electrochem. Soc.* **104,** 29 (1957).
*151.* Zakharkin, L. I., and Gavrilenko, V. V., *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* p. 2246 (1961).

*152.* Zakharkin, L. I., and Gavrilenko, V. V., *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* p. 1146 (1962).
*153.* Zakharkin, L. I., and Gavrilenko, V. V., *Dokl. Akad. Nauk SSSR* **145,** 793 (1962).
*154.* Zakharkin, L. I., Gavrilenko, V. V., Khorlina, I. M., and Zhigareva, G. G., *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* p. 1872 (1962).
*155.* Zeigler, K., *Angew. Chem.* **64,** 323 (1952).

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