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A SURVEY REPORT ON LITHIUM HYDRIDE

By
Charles E. Messer

October 27, 1960

Tufts University
Medford, Massachusetts

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ABSTRACT

The physical and chemical properties of lithium hydride are described, based on reasonably full coverage of the available unclassified literature as of July 1, 1960. Where possible, the data are presented critically. Lithium deuteride and lithium hydride gas are included. Practical matters such as thermal stability, corrosive character, utilization, handling, fabrication, and analysis are discussed. This report replaces the older reports, NYO-3957 and its supplement, NYO-8022.

ACKNOWLEDGEMENT

The author wishes to express his deep indebtedness to Professor Thomas R.P. Gibb, Jr. for his advice and suggestions on this revision of our earlier versions of this report, and for his contributions to the earlier versions which have been retained in the present report except where they have had to be modified by recent developments.

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INTRODUCTION

This report is intended to be an essentially complete survey of the unclassified literature on the fundamental properties of lithium hydride. It replaces the older survey reports NYO-3957 (1) and NYO-8022 (2), and brings them up to date as of about July 1, 1960. All information from these older reports not known to be outdated has been included, although it has not been possible in some instances to check the obsolescence of certain purely technological information.

The report is written from the chemical point of view. While nuclear applications are always kept in mind, data on the nuclear properties of lithium hydride as such are not included because this laboratory is not qualified to evaluate these aspects.

The properties of lithium hydride which are discussed are: preparation, physical and thermodynamic properties, chemical reactivity, and thermal stability. Related practical considerations such as handling, fire hazards, toxicity, fabrication, and analysis are included. Critical comparisons of conflicting literature results is made where appropriate. Predictions of certain properties such as high temperature density and heat capacity have been made where sufficient data were available. These are not rigorous and should be carefully differentiated from the results of actual experiments.

The topical outline and the reference number systems in this report have been completely changed as compared with the older versions, NYO-3957 and NYO-8022.

100 General Considerations on LiH

Lithium hydride is of interest because of its low density combined with high radiation and thermal stability. Its relatively high value of $N_H = 5.90$ ($\times 10^{-22}$ H atoms per cm^3) makes it of interest as a lightweight neutron moderator, and its high active hydrogen content as a fuel.

It is reactive to air and moisture, but in a closed container or in an inert atmosphere may be handled readily and fabricated by melting or compression. Because of its low hydrogen dissociation pressure - 28 mm. at 700°C . (3) - it may be heated to red heat in a thin-walled container without a pressure shell. It is readily combustible and ignites at red heat in air, burning quietly but with intense heat. Careful attention to factors affecting the purity of this hydride are essential, the presence of certain impurities adversely affecting its thermal stability in a sealed container and its corrosive character.

1.01 Classifications and General Description

Lithium hydride is a salt-like white crystalline substance (face-centered cubic) physically resembling a halide and considerably more dense than lithium metal. It is probably less ionic than, for example, sodium chloride, owing in

part to the strong polarization of the negatively charged hydride ion by the smaller lithium ion. Although less ionic, it is a better conductor of electricity than sodium chloride well below melting temperature. Electrolysis of the solid at dull red heat gives hydrogen at the anode.

As ordinarily prepared by the action of hydrogen on molten lithium metal at about 700°C., it forms as a fluid melt which crystallizes in cooling below the melting point of 688° (3). By employing pure lithium and hydrogen and a scrupulously cleaned container, a mass of large colorless cubes may be formed on slow cooling. Optically clear single crystals have been grown by the Stockbarger technique by Pretzel (4).

As ordinarily prepared, lithium hydride is colored due to the photosensitivity of the white crystals, to impurities, or to incomplete hydrogen absorption. The typical color is blue-gray, which is characteristic of the formation of F-centers as in potassium bromide.

Lithium hydride in the form of large crystals or lumps may be handled briefly in air of low humidity but a thin layer of hydroxide and carbonate forms at once. The surface of a crystal freshly exposed to air may be observed under the microscope to become coated with a fluid film which subsequently solidifies and protects the crystal from further rapid action. The hydride is easily powdered under a dry nitrogen or argon atmosphere but in air the fine powder absorbs moisture, carbon dioxide and probably oxygen very rapidly. Exposure of fine powder to humid air or moisture may result in ignition. Crystals coated with hydroxide, etc. will irreversibly evolve a small volume of hydrogen on heating presumably due to the reaction: $\text{LiOH} + \text{LiH} \rightarrow \text{Li}_2\text{O} + \text{H}_2$.

With water a vigorous reaction occurs yielding hydrogen and lithium hydroxide. The latter is basic and sparingly soluble hence in a limited volume of water the reaction tends to slow down because of the accumulation of base and precipitate and to accelerate because the temperature of the water increases. The net results is a fairly steady evolution of gas considerably more rapid than from calcium carbide of comparable dimensions. The finely powdered hydride reacts explosively with water and ignites when moistened. Lumps generally do not ignite when moistened unless they are porous.

On heating, pure lithium hydride discolors slightly and develops an equilibrium pressure of hydrogen which is negligible below dull red heat. The relation of pressure to temperature and hydrogen content is to be discussed in a subsequent section. Lithium hydride seems to be the only saline hydride which melts under a hydrogen pressure of 1 atmosphere or less without decomposition. Melting is accompanied by an expansion of 16% or so in volume (5), but the substance when first melted may appear to contract because of the filling in of the space between particles in the crystalline mass.

The melt is probably not as corrosive as originally believed, since pure hydride may be melted repeatedly in specially cleaned iron and stainless steel

containers without apparent attack. Exposure to air results in the formation of a film of lithium hydroxide or oxide which protects the crystal from further rapid action, but is responsible for highly increased corrosiveness of the melt toward metals.

Chemically, lithium hydride shows many of the reactions of lithium, but less vigorously. At ordinary temperatures it is a much weaker reducing agent towards inorganic oxides, halides, etc. and when dropped into aqueous or alcoholic solutions it fails to effect many reductions which are easily accomplished by lithium metal. It is a basic condensing agent towards aldehydes and ketones and has only weak reducing properties. Unlike lithium, it does not appear to react with nitrogen at ordinary temperatures. With gaseous ammonia it slowly forms the amide at room temperature.

In the metallurgical sense, lithium hydride is a less powerful reducing agent at low temperatures than lithium metal, because of its negative free energy of formation from the metal. At bright red heat, dissociation occurs and the metallurgical properties are those of hydrogen plus lithium. Many metals are reduced at or above red heat, lithium oxide being formed because of its high negative free energy of formation. This oxide is extremely corrosive toward container materials.

Lithium hydride dissolves in molten halides such as the LiCl-KCl eutectic and in certain molten saline carbides. It reacts to some extent with mercury and low melting lead alloys, forming hydrogen and amalgams. Molten lithium hydride is also a solvent for some carbides and halides. There appears to be no inert liquid solvent, although vestigial solubility in ethers has been suggested as a mechanism for the reactivity of lithium hydride in certain reactions (6).

The hydride may be dispersed in most hydrocarbons, ethers, unreactive alkyl halides, esters without α -hydrogens, and tertiary amines. It is compatible with many plastic monomers and polymers, but frequently causes bubble formation when traces of moisture, peroxides, or acidic materials are present.

Lithium hydride may be pulverized and compressed (inert atmosphere) to a hard glossy white compact (which resembles the common life-saver candies) and which has theoretical density.

1.02 History and General Bibliography

Troost and Hautefeuille in 1874 (7) probably were the first to study the reaction of lithium metal with hydrogen, but at their maximum temperature of 500°C. obtained only slight absorption. In 1896 Guntz (8) first prepared the near-stoichiometric hydride and characterized it by measuring some of its properties. Moissan (9) and Dafert and Miklauz (10) (11) studied many of its reactions. Large variations in analysis were reported by the early workers, and even since 1920 many attempted preparations have shown a hydrogen-lithium ratio less than 1:1.

The salt-like character of lithium hydride was recognized by Lewis (12) who noted that the hydrogen had evidently acquired an electron, making it analogous to a halide ion. Moers (13) and subsequently Peters (14) showed that the electrolysis of molten lithium hydride resulted in hydrogen evolution at the anode. The melting point of lithium hydride was first observed by Guntz (15) as 680°C . The most recent value is that of Messer et al (3) of $688 \pm 1^{\circ}\text{C}$.

The following compendia constitute a general bibliography of earlier work on lithium hydride.

Gmelin, Handbuch der Anorganischen Chemie, Vol.20, Verlag Chemie, Berlin, 1927, pp.71-76.

Mellor, J.W., A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. II, Longmans Green and Co., New York, 1922, p. 481.

Hurd, D.T. Chemistry of the Hydrides, Wiley, New York, 1952, pp. 27-30.

Emeleus, H.J. and Anderson, J.S., Modern Aspects of Inorganic Chemistry, Van Nostrand, Princeton, N.J., 1960, Chap. 11.

Sidgwick, N.V., The Chemical Elements and Their Compounds, Vol. I, Oxford Press, London, 1950, pp. 21-22, 66-67.

Anderson, K., Lithium Hydride, NEPA-547, May 25, 1948: Nuclear Science Abstracts 3, 2119.

Nash, C.P., Abstract Compendium on Lithium Hydride, TID-5254 Sept. 27, 1954; Declass.Mar.14,1958; Nuclear Science Abstracts, 12, 6441.

A Bibliography on the Hydrides of Metals and Metalloids, Metal Hydrides, Inc., Beverly, Mass., 1952.

1.03 Sources and Industrial Utilization

The commercial hydride is prepared ordinarily by the action of hydrogen on the metal. The following are believed to be the primary commercial producers of technical lithium hydride:

Foote Mineral Company, 418 Eighteen West Cheltenham Building, Philadelphia, 44, Penna.

Lithium Corporation of America, Minneapolis 1, Minnesota and Bessemer City, North Carolina.

Maywood Chemical Works, Maywood, New Jersey.

Reagent grade lithium hydride does not seem to be on the market, but each of the above suppliers furnishes a "low sodium" grade of lithium metal which is considerably purer than the ordinary commercial metal, which may be used to synthesize purer hydride.

The Foote Mineral Company also offers dispersions of lithium in certain hydrocarbon solvents.

Metal Hydrides, Inc., Beverly, Mass., is a secondary producer, carrying out the hydriding operation only. This Company has also produced experimental quantities of an inseparable mixture of LiH with MgO under hydrogen (16) (17).

American Potash and Chemical Corporation, 3000 W. 6th St., Los Angeles 54, Calif., produces lithium metal but does not seem to produce the hydride.

Several references to the preparation of high purity lithium by vacuum distillation appear in the literature (18) (19) (20) (21), but this material does not seem to be offered on the market.

Both lump hydride and powder are available. Assays of the commercial material run from 95 to over 98% LiH.

The commercial lithium metal and the hydride prepared therefrom are sometimes contaminated with carbon, as graphite or as Li_2C_2 , by a brownish material which occurs in marble-like veins (in the metal), by other alkali metals, chloride, and by the products resulting from exposure to air (oxide, hydroxide, carbonate). The commercial hydride will ordinarily contain the same impurities although not in the same proportion. Thus, some of the alkali metals are removed by the 700°C . treatment with hydrogen, distilling out of the charge as the lithium is hydrided. The commercial hydride is usually gray and resembles calcium carbide or slate in appearance. Part of this coloration may be due to traces of colloidal metal or F-centers. Analyses (by hydrogen evolution) usually run over 98% LiH. Since the evolution method of analysis is not sensitive to lithium content, up to 3 or 4% lithium metal may be present. (See section on analysis). So far as may be ascertained, vacuum-distilled lithium is not used in manufacturing commercial hydride, nor is vacuum-distilled lithium metal available through ordinary commercial channels.

The major commercial use of lithium hydride seems to be the manufacture of lithium aluminum hydride, LiAlH_4 , which is widely used as a reducing agent in the pharmaceutical industry. This process is wasteful of lithium since three-quarters of the lithium goes to lithium chloride in a form difficult to work commercially. Lithium borohydride, LiBH_4 , is also made from the hydride, and one process for the manufacture of diborane uses LiH as a starting material. The magnitude of this latter use is difficult to ascertain, but is presumably considerable and may well be the largest outlet. (Callery Chemical Co. and Olin-Mathieson Chemical Corp.).

Lithium hydride is also used in the manufacture of a few organic chemicals, etc., as a drying agent, as metallurgical reagent, and for the manufacture of lithium amide. These uses are small for the most part.

It is used as a portable lightweight, low pressure source of hydrogen (by reaction with water) for balloons (22) and for other purposes, e.g., pressurizing of fuel tanks. It has been suggested as a storage medium for hydrogen for use in fuel cells (23).

1.04 Standard Preparation of Lithium Hydride

The best available method is direct synthesis from the elements. No other way has been reported as a preparative method. The following directions may be used to obtain white crystalline material of 99% purity or better depending on the purity of the lithium metal used.

Clean a crucible or boat of 316 or 347 alloy stainless steel, bake dry and partially fill with lithium cut in an argon atmosphere. (Carbon dioxide may be used with less satisfactory results but definitely not nitrogen, which reacts rapidly with lithium at room temperature to form the dark nitride). Place the boat anaerobically in a stainless steel retort. Evacuate, heat to 100°C. in vacuum. Admit hydrogen (purified by passage over uranium turnings, or other getter) at atmospheric pressure. Raise the temperature to 750°C. for two hours. Cool in hydrogen, purge with dry argon, open retort and drop boat in a large volume of pure methyl alcohol. This procedure effectively removes lithium-soluble impurities. When boat is clean, rinse in methyl alcohol and ether. Dry and place in argon-filled drybox. Refill with purest available lithium previously washed with petroleum ether, etched in hexane containing a few drops of methyl alcohol, and rinsed in dry hexane.

Transfer anaerobically to the retort, evacuate to 0.01 mu and heat to about 200°C. After one-half hour admit purified hydrogen and heat to 720°C. The cycle, if properly performed, results in removal of sodium and potassium which condense as fluffy pyrophoric hydrides on the cool portions of the retort. When hydrogen absorption ceases, lower the temperature to 690°C. and then allow the retort to cool very slowly between 690 and 680°C. Hold the temperature at 680°C. until no further hydrogen absorption occurs, then cool slowly to 500°C. and again hold the temperature until no further absorption occurs (over night, if necessary). Cool in steps of 100°C., noting any small absorption of hydrogen. When at room temperature, purge with dry argon or nitrogen and remove quickly, preferably anaerobically to a nitrogen or argon-filled drybox. The mass of large crystals may be iridescent on the upper surface, which is scraped clean. The balance of the material is readily detached by tapping the boat and should be white clear crystals of lithium hydride. The purity and appearance will vary with the purity of the starting materials. Larger crystals may be obtained by using a similarly cleaned pure iron crucible of the Stockbarger type (conical bottom) and a thermal gradient technique. The iron becomes very brittle after cleaning and must be handled with great care. (**Iron** is used because of its permeability to hydrogen).

The manufacture of lithium hydride is briefly described in a literature reference to the lithium operations of Lithium Corporation of America (24).

Recent attempts to improve the low-temperature oil-dispersion synthesis of lithium hydride have been reported by the Olin-Mathieson Chemical Corporation (25) and by Seep (26). Here, the liquid lithium is reacted with hydrogen dispersed in oil in the presence of a catalyst.

Ponomarenko and Mironov (27) have described a modification of the standard preparation, based on an improvement of the earlier work of Albert and Mahe' (28).

Large single crystals have been grown by the Stockbarger technique by Pretzel (4).

Suspensions of lithium hydride in hydrocarbons have been prepared in concentrations up to 15% by Ziegler et al (29), and an attempted preparation in glycol ether at 180°C. is reported. (230)

References to the kinetics of formation of lithium hydride, Sec. 3.01, give further information on conditions of preparation.

Other reactions leading to the formation of lithium hydride but not at the moment of interest as methods of preparation are:

2.00 PHYSICAL AND SOLID STATE PROPERTIES

2.01 Crystal Structure

The crystal structure of lithium hydride is face-centered cubic, of the sodium chloride type. The lattice constant was first carefully determined by Zintl and Harder (40), and later by Tronstad and Wergeland (41), Ahmed (42) (43), and Zalkin (44). The most precise value seems to be that of Staritzsky and Walker (45):

$$a_0 = 4.0834 \pm 0.0005 \text{ A.U.}$$

The earlier value of Bijvoet and Karssen (46) of 4.10 A.U. is slightly in error, due to the admitted contamination of the sample by exposure to air.

The hydrogen atoms in a hydride cannot be located directly by X-ray diffraction methods. According to the early X-ray scattering results of Bijvoet and Karssen (46) (47), the wurtzite or ZnS structure was theoretically possible as an alternate interpretation of the X-ray scattering intensities. The later studies, however, favor the NaCl structure definitely (40) (42) (48). The early work of Bijvoet and Karssen has been criticized by Zintl and Harder (49) (50).

The hydrogen atoms in a crystal lattice may be located by neutron diffraction, and the fact that sodium hydride, NaH, has the sodium chloride structure has been verified definitely by neutron diffraction (51). Lithium hydride has not yet been investigated in this way.

Lonsdale (52) has calculated the root-mean-square amplitude of vibration of the atoms in solid lithium hydride at 20 C. from the X-ray scattering data and from the Debye Θ . The value for lithium hydride is 0.24 A.U.

2.02 Density

The density of lithium hydride has been determined in several ways. Moers (13) and Bode (53) measured the density by means of a pycnometer. Hexane was used as the displacement liquid; in both cases the hexane was dried by means of sodium metal and also some of the lithium hydride.

The density of lithium hydride was also determined in this laboratory (results as yet unpublished) by means of the helium densitometer (54). This apparatus effectively determines the volume of the sample from the amount of helium gas displaced by it.

The density may also be calculated from the known lattice constant, crystal structure, and molecular weight. The values of density and molar volume determined by each of these methods are summarized in Table 1 below.

Table 1
Density and Molar Volume of Lithium Hydride

	<u>d, g./ml.</u>	<u>V_m, ml./mol</u>
Pycnometer, Moers (13)	0.816 $\pm$ 0.004	9.74
Pycnometer, Bode (53)	0.705 $\pm$ 0.02	11.27
He Densitometer, this lab.	0.788 $\pm$ 0.002	10.08
X-ray Crystallographic (45)	0.775 $\pm$ 0.001	10.254

The pycnometric technique obviously leads to highly varying results, being subject to errors due to trapped bubbles of gas as well as to the ever present error of hydrolysis products. The recommended value, based on the X-ray crystallographic and helium densitometer, is:

$$d = 0.780 \pm 0.007 \text{ g./ml.}$$

Further research is needed to define the density more precisely.

2. 2.021 Coefficient of Expansion and High Temperature Density

Laquer (55) measured the coefficient of expansion of lithium hydride over the range from 20°K to 300°K by a dilatometric technique, determining the change in length of a pressed specimen relative to its length at 273°K. His results were uncertain to $\pm 10\%$, due apparently to exposure of the sample to atmospheric moisture during handling.

The coefficient of expansion at high temperatures was determined by Zalkin (44), who measured the lattice constant from 25°C. to 525°C. by X-ray diffraction. His results may be expressed by the equation:

$$a_0 = a_0(25^\circ\text{C}) [1 + 4.2 \times 10^{-5}(t-25) + 1.9 \times 10^{-8}(t-25)^2]$$

This gives a linear coefficient of expansion of $4.2 \times 10^{-5}/^\circ\text{C.}$ at 25°C., or a cubical coefficient of $1.26 \times 10^{-4}/^\circ\text{C.}$ These agree closely with a previous estimate of Nordmann and Lipscomb (56) of 3.9×10^{-5} and 1.2×10^{-4} , respectively, based on lattice frequency considerations. They are also very close to the values for sodium chloride (cubical coeff. 1.21×10^{-4}).

Fieldhouse, Hedge, and Lang (57) have measured directly the linear coefficient of expansion of a rod of lithium hydride, from room temperature to 650°C. Their results agree closely with those of Zalkin up to Zalkin's highest temperature of 525°C. At higher temperatures their expansion coefficients seem to decrease rather than increase in the normal way, suggesting possible sintering of their sample. Hence, the estimates to follow are based upon the extrapolation to higher temperatures of the data up to 525°.

The density of lithium hydride has been calculated up to 525°C. and estimated at higher temperatures, and the values are given in Table II.

Table II
Density and Lattice Constant of Lithium Hydride

<u>t°C.</u>	<u>a° A.U.</u>	<u>d, g/cm³</u>
25	4.083	0.775
200	4.116	0.757
400	4.159	0.733
525	4.188	0.718
600	(4.21)	(0.705)
688 (s)	(4.24)	(0.69)
688 (l)		(0.58 $\pm$ 0.03)

The solid densities at 600° and 680° were adjusted for the fact that the coefficient of expansion tends to increase more rapidly than the extrapolated estimate at temperatures approaching the melting point.

The percentage increase in volume on heating from 25°C. to the melting point is 12. This is in the range of values for the alkali halides, 12-16% (58).

From considerations on volume changes on melting as a function of chemical bonding in the crystal, the density of the liquid at 688°C. is estimated at 0.58 ± 0.03 g/cm³.

(Details of Method of Estimation of Liquid Density:)

If lithium hydride were purely ionic, it should expand about 26% on fusion, as judged by the experimental values for LiF, LiCl, NaF, and NaCl which range from 25% to 29% (58).

The effect of covalency is shown by silver bromide and silver chloride, which expand only 8% and 9%, respectively, on melting (58).

The percentage change of volume on fusion was graphed against the degree of covalency of bonding for lithium and sodium compounds with the sodium chloride structure, the degree of covalency being estimated by the method of Pauling (59) from electronegativity differences. The indicated value for lithium hydride from this graph was between 16% and 20%.

Silver chloride and bromide have about the same electronegativity difference as lithium hydride, but Pauling considers (59) that they are actually much more covalent than electronegativities alone would indicate because of the tendency toward complexes as AgCl_2^- .

The intermediate position of lithium hydride in degree of covalent bonding is thus supported, and the volume increase of 18% on fusion is suggested as representative of this position.

McKisson (5) reports a density of 0.76 g/cm³ for lithium deuteride at 720°C. If it is assumed that the molar volumes are in the same ratio for LiH and LiD as at 25°C., the density of 0.67 g/cm³ is obtained for lithium hydride at 720°C. The discrepancy between this value and the estimated value is far greater than the errors of estimation. Only if the expansion of lithium hydride on fusion turned out to be even less than that of silver chloride could the two values be reconciled.

2.022 Compressibility

The coefficient of compressibility of lithium hydride has not been obtained experimentally. Kasarnowsky (60) and Sherman (61) report a value based on the Born repulsion coefficient from lattice energy calculations:

$$k = 2.32 \times 10^{-12} \text{ c.g.s. units}$$

This is of the same order of magnitude as the values for the alkali halides: e.g., 4.18×10^{-12} for NaCl and 1.53×10^{-12} for the more closely comparable LiF.

2.03 Electrical and Magnetic Properties

2.031 Electrical Conductivity and Electrolysis

G.N.Lewis (12) first suggested, on the basis of his electronic theory of valence, that the hydrogen in lithium hydride should be anionic, taking on an electron to form the hydride ion, H^- , with the two electron stable configuration of the helium atom. Hence, lithium hydride should be salt-like in nature. Preliminary experiments under his direction indicated that fused lithium hydride (m.p. $688^\circ C.$) is a good conductor of electricity.

Moers (13) measured the electrical conductivity of lithium hydride at temperatures from $443^\circ C.$ to $754^\circ C.$, using both direct and alternating current, but obtaining consistent results only with the latter. Table III below shows his results.

Table III
Electrical Conductivity of Lithium Hydride

<u>$T^\circ C.$</u>	<u>443</u>	<u>507</u>	<u>556</u>	<u>597</u>
Sp. Cond., ohms ⁻¹ cm ⁻¹	2.124×10^{-5}	2.154×10^{-4}	9.633×10^{-4}	3.665×10^{-3}
<u>$T^\circ C.$</u>	<u>657</u>	<u>685</u>	<u>725</u>	<u>754</u>
Sp. Cond., ohms ⁻¹ cm ⁻¹	0.01811	0.03607	0.09213	0.1796

These data may be represented to $\pm 5\%$ by the empirical formula:

$$k = 2.065 \times 10^{-4} + 1.8 \times 10^{-7}(T-500)^2 + 1.95 \times 10^{-11}(T-500)^4 + 0.5 \times 10^{-21}(T-500)^8.$$

The temperature coefficient varies from 0.1-0.2% per $^\circ C.$ No discontinuity is noticeable at the melting point of $688^\circ C.$

Guntz and Benoit (62) noted that when lithium carbide, Li_2C_2 , was dissolved in molten lithium hydride, electrolysis occurred. At 0.05 volt, amorphous carbon deposited at the anode; above 0.1 volt, hydrogen gas was liberated at the anode. This indicates that Li_2C_2 is ionized in lithium hydride, which itself is ionized, with H^- as the negative ion.

Peters (14) studied the application of Faraday's Law to the electrolysis of lithium hydride. He carried out the electrolysis in a V-shaped steel vessel, to separate the anode and cathode electrolysis products, and made corrections for the amount of hydrogen produced by thermal dissociation. He was able, in one run, to obtain up to 99.5% of the theoretical amount of hydrogen

evolved at the anode, but the yields were mostly 80-90%. The highest yields were obtained with solid lithium hydride between 550°C and 650°C., and when the hydrogen pressure was large enough to prevent dissociation of the lithium hydride.

Potter and Bockris (63) also studied the electrolysis of lithium hydride. They found their highest yields of anode hydrogen (over 80%) to occur for short electrolysis times (2.5 minutes) and at temperatures just under the melting point (688°C). At higher temperatures, or for longer times, the yield decreased.

Weinberger, Mousseau, and Maass (64) were able to obtain a current yield of 70% in continuous electrolysis at or below the melting point. They used a molten aluminum cathode as a scavenger electrode. The deposited lithium metal dissolved in the aluminum, which kept it out of contact with hydrogen gas, preventing the back reaction.

2.032 Dielectric Constant

This quantity has not been measured, but may be calculated from other properties. The high frequency dielectric constant is 3.60 from the refractive index at infinite wave length (45). The static dielectric constant $\epsilon_0 = 12.5-13.0$ from observed infrared optical frequencies (65) (66).

2.033 Magnetic Susceptibility

The magnetic susceptibility was measured by Freed and Thode (67). The substance is diamagnetic, with $X = 4.6 \times 10^{-6}$ cgs units per mole at 300°K. Variations of a few percent were found among different batches, and an increase of 1.1% was found on cooling to 78°K. This increase can be accounted for by a paramagnetic impurity of about 0.35%, quite possibly due to lattice defects.

The experimental value is considerably lower than theoretical predictions. Koppe (68) gives a calculated value of $X_{\text{mol}} = -11.8 \times 10^{-5}$, based upon the molar susceptibility as the sum of the ionic susceptibilities in a lattice with only He-type ions. Freed and Thode attribute the low experimental value to "fluctuation paramagnetism due to deviation of instantaneous angular momentum from zero".

2.04 Optical Properties

2.041 Refractive Index

Staritzsky and Walker (45) have measured the refractive index of lithium hydride by the refraction of prisms ground from crystal fragments. Their value at 25°C. is:

$$n_D = 1.9847$$

This is much higher than Bode's (53) earlier value of 1.615 by the immersion method. Refractive indices at other wave lengths, molar refractions, and molar dispersions are also given (45) (69).

2.042 Infrared Absorption

From reflection measurements from 2.50 μ , Filler and Burstein (65) found a strong reflection peak in the region from 550-1100 cm^{-1} . They interpreted this as indicating a longitudinal optical frequency of 1120 cm^{-1} for LiH.

Zimmerman and Montgomery (66) studied the absorption of LiH from 12-25 μ . They found an absorption peak at 17.0 μ , interpreted as due to the transverse optical frequency of 590 cm^{-1} .

2.043 Ultraviolet Absorption Spectrum

The absorption spectrum of crystalline lithium hydride in the ultraviolet was observed by Kapustinsky, Shamovsky, and Bayushkina (70) (71) and by Bach and Bonhoeffer (72) (73). Both groups of workers found a sharp absorption maximum at 2517 ± 2 A.U. In addition, Bach and Bonhoeffer observed a diffuse absorption band, beginning at 1900 A.U. and extending to shorter wave lengths.

Rauch (74) studied the ultraviolet absorption of a thin film of lithium hydride made by bombarding a thin film of lithium metal with atomic hydrogen. He found no absorption above 250 μ , then gradually rising absorption down to the lowest wave length studied, 186 μ . He calculated the energy of this band maximum as 7.61 e.v., corresponding to a predicted peak at 163 μ .

Lithium hydride also shows a visible-near ultra-violet absorption spectrum, and a corresponding emission spectrum, when heated above 750°C. These are due to the presence of gaseous LiH molecules, and will be discussed in Section 7.00.

2.044 Photochemical Behavior

When exposed to daylight at room temperature, lithium hydride is observed to change slowly in color from white to rose, brown, and finally to gray-blue (13) (72) (73) (11). Ultraviolet light produces the blue color more rapidly. No measurable hydrogen loss by decomposition is noticeable, although it is reported (13) that cracks and fissures are noted on the surface which are not present on the white crystals.

The coloration lasts indefinitely at room temperature, but disappears at 70°C. (73). Albert and Mahe (28) noted that the blue lithium hydride changed back to white on heating at 690°C. in hydrogen, while evacuation at 650° brought back the blue color. Ionic bombardment at room temperature also produced the blue color.

These facts are readily interpreted in terms of a reversible slight decomposition of lithium hydride into hydrogen and lithium metal, which produces the color. The amount of decomposition is too small to be detected analytically.

Bach and Bonhoeffer (72) (73) have investigated the process using photochemical techniques. They studied the amount and rate of hydrogen evolution produced by known light intensities, using the 2537 A.U. line. The quantum yield was about 5%.

The photochemical process occurring at 2517 A.U. is undoubtedly the transfer of an electron from anion to cation in the lattice, by analogy to the alkali halides (70) (71) (72) (73):

The absorption occurs at the wave length predicted by the quantum theory for this process. The second band is near 1830 A.U., which is the wave length predicted for the breakdown of crystalline LiH into excited Li atoms and normal H atoms (73).

Pretzel (4) has studied the optical absorption effects on irradiation of single crystals of lithium hydride grown from the melt under hydrogen. A band due to F centers (hydrogen vacancies) is found at 2.19 ± 0.02 electron volts at 77°K. X-irradiation at this temperature forms many other bands which obscure the F band. Most of these bands bleach out quickly at room temperature.

A band due to colloidal lithium was shown to form readily at room temperature in samples containing 10^{16} or more F centers per cm^3 . Also, there seems to be a slow change of colloidal lithium to F centers at room temperature.

Doyle, Ingram, and Smith (75) have also studied the effects of irradiation of LiH with ultraviolet radiation of 2537 A. They found a strong optical absorption band at 650 mμ. The interpretation of the position of this band, plus electron resonance studies on the irradiated crystals, led to the conclusion that the band was due to colloidal lithium.

Gavrilov (76) observed an orange-red luminescence when lithium hydride was irradiated with the 3650 A mercury vapor line. Three maxima were found at 5970 A, 6550 A, and 7180 A. Chemical analysis showed 0.4% excess Li, to which the luminescence was attributed. The production of the effect in crystals activated by Au or Mg is also discussed.

3.00 THERMODYNAMIC AND THERMAL PROPERTIES

3.01 Heat of Formation

The heat of formation of lithium hydride has been measured by means of the

difference between the heats of hydrolysis of the hydride and of lithium metal, both measured in the same calorimeter with the same technique.

These heats have been measured by Guntz (15), Moers (13), Messer, Fasolino, and Thalmayer (77), and Gunn and Green (78). The results are given and compared in Table IV.

Table IV
Heats of Hydrolysis and Formation of Lithium Hydride

<u>ΔH, kcal/mole at 25°C., infinite dilution</u>		
	<u>Heat of Hydrolysis</u>	<u>Heat of Formation</u>
Guntz (15)	-31.6	-21.6
Moers (13)	-31.1	-21.6
Messer, Fasolino, and Thalmayer (77)	-31.76 ± 0.06	-21.34 ± 0.12
Gunn and Green (78)	-31.476 ± 0.018	-21.666 ± 0.026

The measurements of Guntz and of Moers were made in open Dewar Flask calorimeters, the hydrogen gas being allowed to escape. Those of Messer, Fasolino, and Thalmayer and of Gunn and Green were carried out in a closed bomb calorimeter, the hydrogen evolved thus being confined.

3.02 Heat Capacity

The heat capacity of lithium hydride has been measured by Guenther (79) over the comparatively narrow low temperature range from 74°K. to 90°K., and also at room temperature, 293°K. As shown by Ubbelohde (80), these data fit fairly well a Debye heat capacity curve, with the characteristic temperature $\theta = 815 \pm 10$. The 20°C. values are:

$$C_p = 8.177 \text{ cal./mol-deg.}$$

$$c_p = 1.029 \text{ cal./gram-deg.}$$

Lang (81) has measured the enthalpy of lithium hydride from room temperature to 641°C. by means of a drop calorimeter, enabling the derivation of high temperature specific heats. The enthalpy is represented by the following formula from 80°-1050°F:

$$H_T - H_{80} = -59.17 + 0.8475T + 0.3989 \times 10^{-3}T^2, \text{ BTU/lb., } T = ^\circ\text{F.}$$

At higher temperatures, experimental values deviate positively from this formula.

By differentiation, this gives for the specific heat:

$$c_p = 0.8475 + 0.7978 \times 10^{-3}T, \text{ BTU/lb } ^\circ\text{F} = \text{cal/g}^\circ\text{C., } T = ^\circ\text{F}$$

Messer and Gibb (2) made an estimate of the high temperature heat capacity of LiH, based on analogy with the known heat capacity of lithium fluoride (82).

Theoretical-empirical equations were set up for the heat capacity of lithium fluoride, and deviations of the predicted values from the experimental values were noted. The corresponding expressions for lithium hydride were set up, and it was assumed that the deviations followed the same pattern as for lithium fluoride.

Table V shows a comparison of these heat capacity values at several temperatures. Two sets of values are given for Lang's data because his graphical and formula values seem to differ.

Table V
Heat Capacity Values for Lithium Hydride, Cal/Mole °C.

T°K.	T°C.	T°F.	Messer and Gibb (2) estimated	Lang (81)	
				Formula	Graphical
298	25	77	8.2 (ref. 79)	7.2	(7.8)
500	227	441	11.2 ± 0.3	9.5	9.9
800	527	981	13.5 ± 0.7	12.9	12.9
961 (s)	688	1270	14.8 ± 1.0	---	---
961 (l)	688	1270	15.5 ± 1.0	---	---

Lang's graphical values agree reasonably well with the estimated values of Messer and Gibb. Probably the greatest reason for the discrepancy is that the heat capacity behavior of LiH is too complicated to be well represented by the simple linear temperature dependence which works so well for so many compounds. Below about 800°K., this substance is still acquiring its full classical (Dulong and Petit) heat capacity of about 13 cal/mole°, with the temperature coefficient of the heat capacity decreasing with increasing temperature. Above this temperature, the typical behavior just below the melting point is for the temperature coefficient of the heat capacity to rise. The fitting of Lang's enthalpy data to a more complex function of temperature might improve the specific heat values and make them conform better to the general type of behavior found for simple ionic substances.

(Details of Estimation of Heat Capacity, Messer and Gibb)

The relations used were: $C_p = C_v + (C_p - C_v)$, $C_v = 6D(\theta/T)$, $C_p - C_v = AC_v^2T$ or $BT^{3/2}$. Debye characteristic temperatures were taken as 648 for LiF and 920 for LiH. $C_p - C_v$ was calculated at 25°C. for both compounds from published values for molar volumes, coefficients of expansion, and coefficients of compressibility, and the 25°C. values were used to determine the constants A and B. The experimental values of 8.2 cal/mole-deg. for LiH (79) and 10.02 for LiF (82) were used for heat capacities at 25°C. In this way all constants were chosen for exact agreement with the 25°C. experimental data.

The heat capacity of liquid LiH was taken as the same as that of liquid LiF, 15.5 cal/mole-deg. This assumes that liquid salts of a given structure type tend to have heat capacities which are nearly alike and almost temperature independent, as is the case for liquid metals (83).

3.03 Entropy, Free Energy of Formation

Kelley (84) has calculated the entropy of lithium hydride at 298°K, from Guenther's (79) heat capacity data. The free energy of formation may then be calculated, using this figure and the heat of formation of Gunn and Green (78). The resulting values are:

$$S^{\circ} 298^{\circ} \text{K.} = 5.9 \pm 0.5 \text{ cal/mole-deg.}$$

$$\Delta F^{\circ} \text{ f } 298^{\circ} \text{K.} = -16,780 \pm 300 \text{ cal/mole.}$$

3.04 Melting Point and Latent Heat of Fusion

The melting point of lithium hydride has been shown to be 688°C. $\pm 1^{\circ}$, or 1270°F.

No calorimetric measurement of the latent heat of fusion has been made. Messer (85) has calculated a cryogenic value from the lowering of the freezing point of LiH by the solutes lithium oxide and calcium hydride, which show identical behavior within experimental error up to 9 mole % solute. This value is:

$$\Delta H_f = 4900 \pm 700 \text{ cal/mole}$$

This gives an entropy of fusion of 5.1 cal/mole-deg., which is within the range shown by the lithium halides (86).

3.05 Latent Heat of Sublimation

Sodha and Varshni (87) have calculated the latent heat of sublimation of LiH from thermochemical and spectroscopic data as 51.6 kcal/mole.

3.06 Thermal Conductivity

Vetrano (88) has reported measurements from 50°C. to 600°C. on two kinds of samples: (a) compacted 3" x 3/4" specimens of density 0.775 g/cm³, and (b) a specimen of cast material. The two sets of results differ considerably, especially at lower temperatures.

Fieldhouse (89) has also measured the thermal conductivity of compacted material over this same temperature range, measuring radial heat flow from inside to outside of a series of stacked annular rings of 5/8" i.d. and 3" o.d.

The results of these researches are shown in Table VI. The values shown are smooth-curve values at selected temperatures.

Table VI
Thermal Conductivity of Lithium Hydride

Watts Cm⁻² cm °C.⁻¹

T°C.	Vetrano, Crystals	Vetrano, Compact	Fieldhouse
50	0.125	0.0695	0.075
100	0.106	0.0652	0.0650
200	0.074	0.0575	0.0576
300	0.055	0.0515	0.0510
400	0.042	0.0469	0.0453
500	0.036	0.0432	0.0414
600	---	0.0409	---

4.00 FORMATION, DISSOCIATION, PHASE EQUILIBRIA

4.01 Kinetics of Formation and Dissociation

The qualitative variation of rate of hydrogen uptake of lithium with temperature was observed by many workers, and the pattern seems to be about the same for all. The reaction of hydrogen with bulk lithium begins at a fairly low temperature, and proceeds at a moderate rate until a certain amount is taken up. This amount varies from a few percent up to 24% of the theoretical. The rate then slows down, and it is necessary to raise the temperature to complete the reaction. Table VII below summarizes the observations of the various workers.

Table VII

	Temp. of first reaction	Temp of rapid reaction
Guntz (8)	Just before red heat	Full red heat
Dafert and Miklauz (11)	440°	700°
Ephraim and Michel (90)	300°	580-660°
Soliman (91)	500°	---
Bode (53)	450-500°	700°
Albert and Mahé (28)	450°	680-690°

The interpretation of this behavior is clear in terms of the dissociation pressure behavior to be described in section 4.02 to follow. During the initial low temperature uptake, the hydrogen is dissolving in molten lithium. When saturation is reached, either throughout the bulk or on the surface, solid lithium hydride forms, slowing down further absorption. The temperature must then be raised to increase the rate, which cannot reach its maximum until the lithium hydride melts at 688°.

There is some evidence that lithium metal will take up hydrogen at a lower temperature under certain circumstances. Remy-Gennete (92) reports that lithium metal, distilled out of contact with air, took up about 9% of the theoretical

amount of hydrogen at room temperature in 24 hours, and about 36% in one month. No significant uptake of hydrogen was noted for the undistilled metal. Huettig and Krajewski (93) report that the finely divided form of lithium metal, prepared by dissolving it in liquid ammonia, reacts with hydrogen at room temperature.

Huettig and Krajewski (93) have studied the rate of decomposition of lithium hydride from 100° to 270°C. The solid sample was introduced into a high vacuum and the rate of pressure increase followed until the pressure became constant. The first significant rate of hydrogen loss was observed at 100°C. Sublimation to cooler parts of the container caused complications above 190° (In view of the fact that the vapor pressure of lithium metal is only about 10^{-10} mm. at 190°C. (21), this sublimate could not have been lithium metal).

The rates varied widely and in an unsystematic way, the times for achievement of the final constant pressure varying from 60 to 885 minutes, most of the values falling between 120 and 240 minutes. The results were further complicated by the fact that in most runs there was an interruption of the heating period, during which the sample was allowed to cool. The pressures involved were mostly between 0.05 and 0.22 mm. Hg.

Quantitative data on the rate of reaction of lithium with hydrogen are relatively scarce. Albert and Mahe (28) report a rate of uptake of hydrogen of 1.5 cm.³ H₂ per cm.² of surface per second, at 1 atm. and 680°C. Perlow (94) also gives some quantitative data on the rate of this reaction, and obtained an activation energy for the reaction of 12.0 ± 0.1 kcal./mol. Some semi-quantitative rate data are given in the references in Table VII, but these do not fit an easily describable general pattern.

Swain and Heumann (95) studied the rate of reaction of hydrogen with lithium at temperatures from 25°C. to 250°C. The initial rate of reaction was directly proportional to the mass of lithium and to the pressure of hydrogen. The rate then fell off, and apparently became diffusion-controlled. Irregularities in rate were shown to be due to the presence of nitrogen in the lithium.

The variation of specific reaction rate constant with temperature was:

$\log k = -1380/T + 2.09$. This gives a heat of activation of 6300 cal/mole H₂.

4.02 Dissociation Pressure

The equilibrium hydrogen pressure over lithium hydride, pure and partially decomposed, varies with both temperature and composition in the manner characteristic of most metal-hydrogen systems. The variation with temperature at constant composition of the phase(s) present normally follows the van't Hoff isochore, as represented by the approximately linear plot of the logarithm of the "Plateau" pressure vs. the reciprocal of the absolute temperature shown in Figure 1. The variation of dissociation pressure with composition at constant temperature is shown in Figure 2.

FIGURE 1

PLATEAU DISSOCIATION PRESSURES
LITHIUM-LITHIUM HYDRIDE SYSTEM

FIGURE 2
DISSOCIATION PRESSURE ISOTHERMS
LITHIUM-LITHIUM HYDRIDE SYSTEM

The explanation of the shapes of the isotherms in Figure 2 is as follows: The dissociation pressure of the hypothetical completely pure stoichiometric lithium hydride is very high--theoretically the limiting value could be infinity. The removal of small amounts of hydrogen produces a large decrease in pressure, with the formation of hydrogen vacancies in the lithium hydride lattice, which remains as a single phase. When enough hydrogen has been removed, the lattice becomes saturated with hydrogen vacancies. Further withdrawal produces a constant pressure, independent of composition, and a second phase, a saturated solution of hydrogen in lithium, begins to separate out. The constant pressure in this two-phase region of varying composition is the so-called "plateau" pressure. When enough further hydrogen has been withdrawn, the hydride phase disappears, and further hydrogen loss produces a decrease in pressure due to loss of hydrogen from solution in the remaining single phase. The pressure finally diminishes to zero at zero hydrogen content (pure lithium).

Some of the earlier measurements of the equilibrium dissociation pressure of lithium hydride gave variable and inconsistent results because the variation of pressure with composition was not realized or not controlled by the workers making the measurements. Hence, the compositions for which the reported pressures were valid are unknown. The dissociation pressure measurements of Ephraim and Michel (90), Tronstad and Wergeland (41) and Peters (14) all gave results higher than the thermodynamically estimated pressures, which are essentially the plateau pressures. This, of course, was because nearly stoichiometric lithium hydride has a pressure much higher than the plateau pressure, and a pressure highly sensitive to small changes in composition.

The dissociation pressure of the lithium hydride-lithium system as a function of temperature and composition has been investigated more carefully by Hill (96), Perlow (94), Gibb (97), and, most recently and carefully, by Heumann and Salmon (98). The isotherms of Hill, Perlow, and Heumann and Salmon are shown in Figure 2. The numerical values for these researches and for that of Gibb are shown in Table VIII. The sample of Hill was 99.7% LiH by hydrogen evolution analysis; the sample of Perlow was 96.5%; that of Gibb was 98.5%. These have been corrected to 100% purity by assuming the impurities to be inert, even though it is recognized that "100%" represents maximum hydrogen absorption under the circumstances rather than completely pure LiH.

The curve of 'Hill is seen to be higher than that of Neumann and Salmon at 700°. It is also seen in Figure 2 that the dissociation pressures of Hill and Perlow at the three temperatures seem to approach each other at a hydrogen content definitely above zero. Hence, these isotherms are less reliable at the lower hydrogen contents.

The plateau pressure of Heumann and Salmon of 28 mm. at 700°C. was confirmed by Messer et al (3).

Table VIII
Dissociation Pressures of the Lithium-Lithium Hydride System

<u>Hill, 700° C.</u>									
Wt. % LiH	2.7	2.7	5.4	8.4	11.5	14.2	16.3	20.2	26.5
P _{H₂} , mm.	13.2	11.0	15.5	19.0	21.0	28.0	29.0	35.0	35.0
Wt. % LiH	52.7	79.2	87.4	97.9	100.0				
P _{H₂} , mm.	35.0	35.0	35.0	35.0	268.0				
<u>Perlow, 770° C.</u>									
Wt. % LiH	2.2	3.5	5.0	7.4	10.6	17.5	23.7	25.6	35.6
P _{H₂} , mm.	14.0	17.5	25.0	34.5	53.5	79.7	119.5	119.5	156.0
Wt. % LiH	50.8	53.3	63.6	67.2	71.6	75.1	81.2	85.6	89.4
P _{H₂} , mm.	152.0	150.0	138.6	145.0	145.0	149.5	163.0	155.5	160.5
Wt. % LiH	92.0	96.3	98.2	99.1	99.7	100.0			
P _{H₂} , mm.	164.0	154.5	161.0	193.0	211.5	317.5			
<u>Perlow, 825° C.</u>									
Wt. % LiH	5.2	7.5	11.3	17.2	28.0	40.3	54.4	64.2	72.7
P _{H₂} , mm.	17.0	29.5	55.0	106.0	246.0	366.0	417.0	428.0	444.0
Wt. % LiH	78.0	88.9	93.2	97.0	97.8	100.0			
P _{H₂} , mm.	442.0	424.0	442.0	487.0	549.0	714.0			
<u>Gibb, P_{H₂}, mm.</u>									
% LiH	100.0	98.9	96.4	91.4	86.4				
800° C.	7727	1432	160	----	----				
900° C.	9141	4467	861	429	559				
1000° C.	13340	8810	3837	2220	1960				
<u>Heumann and Salmon, 700° C.</u>									
Mole % LiH	2.08	3.24	5.44	8.41	12.63	12.41	17.94		
P _{mm}	2.23	1.96	4.00	7.55	14.80	14.90	22.65		
Mole % LiH	18.80	21.14	24.90	27.48	29.53	29.57			
P _{mm}	23.50	25.60	26.50	27.30	26.50	28.70			
Mole % LiH	49.20	69.91	90.18	96.67	97.55	99.11			
P _{mm}	28.90	27.80	30.10	42.50	91.40	144.20			

The Plateau pressures at a series of temperatures have been measured by Hurd and Moore (99), Hill (96), Gibb (97), and Heumann and Salmon (98). The results of these measurements, and the best composite straight line for the log p vs. 1/T graph, are shown in Figure 1. Also, Table IX gives the constants of the equations for the best straight lines for each set of measurements, the plateau pressures at certain selected temperatures, the temperatures at which the plateau pressures are calculated to reach 1 atm., and the plateau composition limits at certain temperatures.

All values in parentheses are extrapolated beyond the temperature range of the experimental data.

Table IX
Plateau Pressures and Compositions
Lithium-Lithium Hydride System
 $\log p = -A/T^\circ K + B$

		Hurd and Moore	Hill	Perlow	Gibb	Heumann and Salmon
	A	9600	10320	9337	8800	8224
	B	11.227	12.165	11.131	10.20	9.9258
$P_{H_2}^{mm}$	600°C.	1.7	2.2	-----	-----	(3.2)
	700°C.	(22.9)	36.2	(34.2)	-----	28
	800°C.	-----	(352)	268	100	180
	900°C.	-----	-----	-----	500	(830)
$t^\circ C. \text{ for } p = 1 \text{ atm}$		(879)	(841)	(859)	(929)	(897)
Plateau Composi- tion Ranges % LiH	700°C.	-----	18-98	-----	-----	26-96
	800°C.	-----	-----	45-95	??-94	(35-92)
	900°C.	-----	-----	-----	??-88	(47-86)

The plateau regions are seen to become shorter with increasing temperature, indicating increasing mutual solubility of hydride and metal. The dissymmetry would indicate that hydrogen is more soluble in lithium metal than metal in molten hydride. The shortening plateaus also indicate the existence of a critical solution temperature above which metal and hydride would mix in all proportions to give a homogeneous melt. Such a point is predicted by Heumann and Salmon's calculations as 997°C.

Heumann and Salmon also calculated high temperature thermodynamic properties of the system from their equations and data, and made similar measurements on lithium deuteride and tritide. The latter results are given in Section 6.

4.03 Lithium-Lithium Hydride Solid-Liquid Equilibrium

This has been investigated by Messer, Damon, Maybury, Mellor, and Seales (3) in the region just below the melting point of lithium hydride. The results are shown in Figure 3. The system resembles the metal-metal halide systems (100).

The removal of hydrogen from lithium hydride down to a composition of about $LiH_{0.98}$ lowers the freezing point of LiH from 688°C. down to a monotectic at 685°C. Further removal of hydrogen results in a two-phase system of essentially constant freezing point, until the hydrogen content has been reduced to $LiH_{0.26}$. The hydride phase then disappears, and further removal of hydrogen lowers the freezing point further.

The solubility of hydrogen in lithium (or lithium hydride in lithium) from 624-685°C. may be presented to $\pm 1\%$ by the equation:

$$\log (n/1 + n) = -3381/T^{\circ}\text{K.} + 2.835$$

where n is atoms H per atom Li. This gives $\Delta H = -15.47$ kcal/mole for the heat of solution of solid lithium hydride in molten lithium saturated with hydrogen.

The full phase diagram of the lithium-lithium hydride system, incorporating the data and hypotheses discussed in this and the previous section, is shown in Figure 4. The α phase is a solution of hydrogen in lithium; the β phase is a hydrogen-deficient lithium hydride. The solubility of hydrogen in lithium at the lower temperatures, and the extent of freezing point depression of lithium metal by dissolved hydrogen (both not determined experimentally) are exaggerated for the sake of clarity.

4.04 The System Lithium Hydride-Lithium Fluoride

This system has been studied by Messer and Mellor (101) by thermal analysis and X-ray crystallography. The system forms solid solutions in all proportions at the melting point, with a minimum at 682°C. and 13 mole % LiF, only about 5° below the melting point of pure LiH. X-ray crystallography indicated one phase only at higher temperatures, and two phases at lower, with a critical solution temperature between 295° and 320°C.

At room temperature, the X-ray crystallographic studies of Messer and Mellor (101) on 50 mole % LiF in LiH and Zintl and Harder (40) on 27 mole % LiF confirmed the existence of two solid phases in the system at 25°C. The lattice constant of the hydride phase was unmodified within experimental error, while that of the fluoride phase was slightly lengthened from 4.027 Å. to 4.035 Å., in the direction of LiH. This would indicate significant solubility of LiH in LiF, but not of LiH in LiF. Thus the solids mix only partially at room temperature, even though both have the same face-centered cubic crystal structure and their lattice constants differ by only 1.4%.

Gibb (97) measured the hydrogen dissociation pressure of 14.6 mole % LiF in LiH with the following results: 800°C; $p = 85$ mm; 900°C: $p = 345$ mm; 1000°C: $p = 2477$ mm. These are below the plateau pressures, as would be expected if there were solubility of LiF in LiH.

Eichelberger (102) studied the thermal stability of 15 mole % LiF in LiH, finding reversible decomposition to begin at 765°C.

4.05 Other Phase Equilibria

Lithium Hydride-Lithium Oxide (LiH-Li₂O);

Messer and Mellor (103) studied the solid-liquid equilibrium diagram from

FIGURE 3
 FREEZING POINT-COMPOSITION, LITHIUM-LITHIUM HYDRIDE SYSTEM
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FIGURE 4
PHASE DIAGRAM (SCHEMATIC)
LITHIUM-LITHIUM HYDRIDE SYSTEM

0-14 mole % Li_2O . A eutectic was found at 654°C . and 9.3 mole % Li_2O , and evidence for solid solubility of Li_2O in LiH to the extent of 1% or less at 654° was presented.

Lithium Hydride-Calcium Hydride (LiH-CaH_2):

Messer and Krol (104) studied the solid-liquid equilibrium in this system from 0-37 mole % CaH_2 . The eutectic was found at 614° and 18.3 mole % CaH_2 . The liquidus curve of this system coincided with that of the system $\text{LiH-Li}_2\text{O}$ (103) within experimental error from 0 to 9 mole % added substance.

Steiger (105) has patented the use of a mixture of calcium and lithium hydrides as a source of hydrogen, by reaction with water, claiming the advantage of smooth, uniform rate of reaction with water as compared with CaH_2 alone. He calls this mixture a "solid solution", but presents no evidence that it is such in the crystallographic sense. The mixture of lithium and calcium metals is hydrided at $400^\circ\text{-}500^\circ\text{C}$., well below the lithium hydride-calcium hydride eutectic.

Lithium Hydride-Titanium and Zirconium Hydrides:

Messer and Levy (106) found essentially no effect of added TiH_2 or ZrH_2 (8 mole % in each case) on the melting point of LiH . This would indicate that the metal-metal interaction in these hydrides was strong enough to offset any tendency to dissolve in molten LiH .

5.00 THEORETICAL AND BONDING

5.01 Lattice Energy by Born-Haber Cycle

The lattice energy was calculated by Kasarnowsky (60) by means of the Born-Haber cycle as -217 ± 7 kcal/mole. As corrected by Sherman (61), the value is:

$$U = -218.0 \text{ kcal/mole}$$

Earlier values of Kasarnowsky of 234 (107) and of Bradley of 245 (108) were incorrect due to use of an erroneous value of the electron affinity of hydrogen.

Various workers have calculated the lattice energy theoretically, and their values will be present later.

Kasarnowsky (60) obtained a Born repulsion coefficient of $n = 4.1$, and Sherman (61) of $n = 4.4$. Baughan (109) showed that the form Be-gr , with $g = 2.12$ for LiH , was superior to the Born expression as a means of representing repulsive energies in ionic crystals.

5.02 Lattice Frequency and Zero-Point Energy

Ubbelohde (80) calculated the Debye characteristic temperature of lithium hydride, and thence the lattice frequency $\nu_{\max}$, from the low temperature heat capacity data of Guenther (79). The values are:

$$\theta_D = 815 \pm 10, \nu_{\max} = 1.575 \times 10^{13} \text{ sec}^{-1}$$

De Groot and Biedermann (110) have made a more detailed analysis of the lattice frequencies of lithium hydride according to the Born crystal dynamics, including both optical and acoustical vibrations.

Stambaugh and Harris (111) found $\theta_D = 851^\circ\text{K.}$ from vibration amplitudes calculated from the temperature coefficient of X-ray scattering. Phillips and Harris (112) later found, by more detailed analysis, that two lattice frequencies were indicated: $\theta_D = 628\text{-}637$ for Li^+ , and 1657 for H^- . They suggested that the motion of the proton in the large H^- shell and that of the small Li^+ in the interstices between the large H^- must be such that there is no coupling, and hence the heat capacity should be the sum of two Einstein oscillators.

Ubbelohde (80) and de Groot and Biedermann (110) calculated the zero-point energy of lithium hydride. Ubbelohde's value from Debye's continuum theory was $E^0 = 1820 \text{ cal/mole.}$ De Groot and Biedermann calculated this quantity in two ways: first, by London's method of quantization of the mean free paths of rigid spheres; and second, by means of Born crystal dynamics, based on the calculated lattice frequencies. The resulting values were: $E^0 = 1120$ and 5490 cal/mole, respectively. This latter very high value is due to the effect of the high frequency optical waves, which do not play a role in the other theories.

5.03 Nature of the Bonding in Crystalline LiH

The high melting point, hardness, electrolytic conductance, and electrolysis behavior of lithium hydride clearly show its ionic nature. However, the results of certain theoretical calculations show a considerable amount of covalency in the Li-H bond in this solid.

If the radius of Li^+ is taken as its normal value of $0.68 \text{ \AA}$ (113), the lattice constant of $4.083 \text{ \AA}$ would indicate a H^- radius of $1.36 \text{ \AA}$, considerably shorter than the value of $1.51 \pm 0.03 \text{ \AA}$ from the other alkali hydrides. This shortening could be interpreted in terms of tighter bonding due to partial covalency. However, Gibb and Schumacher (114) have shown that if Pauling's radius ratio correction (115) is applied, a constant hydride radius of $1.40 \text{ \AA}$ is found for all of the alkali hydrides.

5.031 Quantum Mechanical Studies

Hylleras (116) has calculated the lattice energy and lattice constant

of lithium hydride by thorough, rigorous quantum mechanical methods. In addition to the ionic terms, his wave function also included terms allowing for covalent exchange between lithium and hydrogen, and also for anion-anion exchange between the highly extended hydride ions. This last exchange apparently leads to an attraction between overlapping H^- ions, exchange overcoming electrostatic repulsion. The closest approximation to the numerical calculation gives 218.6 kcal/mole for the lattice energy (Sherman 218) and 4.42 Å for the lattice constant (experimental 4.083). Hylleras believed that a more elaborate wave function would improve the agreement on lattice distance without changing the lattice energy significantly.

Ewing and Seitz (117) also calculated the electronic structure of solid LiH by quantum mechanical methods. They report calculated electron density distributions about the hydrogen and lithium atoms in LiH, and found the effective charges on the ions to be $Li^{+0.35}H^{-0.35}$.

Lundquist (118) calculated the lattice energy and effective nuclear charge, employing a wave function considering overlap up to sixth nearest neighbors. He obtained excellent agreement in the lattice constant, but the low value of 205 kcal for the lattice energy. The effective nuclear charges corresponded to $Li^{+0.72}H^{-0.72}$, but the calculations were not sensitive to charge.

Morita and Takahashi (119) have also made calculations to determine the effect of homopolar binding on the lattice energy, removing the discrepancy between the observed and Lundquist's values.

Hurst (120) has calculated scattering factors for H and Li in the crystal field of LiH. He concluded that the factor for H^- was considerably modified, the effect being due to the contraction of H^- in the field occurring until offset by electron-electron repulsion and increased electronic kinetic energy.

5.032 Studies Based on Scattering Factors.

Several workers have analyzed X-ray and electron scattering from LiH to obtain information on charge distribution, hence degree of ionic character in the bonding, mostly by comparing the experimental scattering factors with those to be predicted from atomic and ionic models.

Bijvoet and Frederikse (48) found effective nuclear charges of $Li = 2.8$, $H = 0.8$, from X-ray scattering factors, based on a Schrödinger model for the electron distributions.

Ahmed (42) (43) calculated effective charges on the ions from X-ray scattering, corrected for thermal scattering by means of Lonsdale's (52) calculation of the root-mean-square amplitude of vibration. He found, assuming Li^+xH^{-x} , that $x = 0.25 \pm 0.25$.

Stambaugh and Harris (111) analyzed the X-ray scattering of LiH from room temperature down to 20°K., and concluded that LiH becomes less ionic at lower temperatures.

Cochran (121) found no better fit for the ionic model than for the covalent.

Pinsker (122), using electron diffraction on this polycrystalline films of LiH deposited by vacuum sublimation, found evidence of partial negative charge on the hydrogen.

Phillips and Harris (112) have made a thorough analysis of Laue-Bragg scattering at room temperature and at 100°K. From electron density distribution, they found 1.96 electrons within 0.71 Å. of the Li nucleus, and 1.63 electrons within 1.33 Å. of the H nucleus. From effective nuclear charge from scattering factors, $Z_{Li} = 2.55e$, and $Z_H = 1.45e$. Either way, LiH has ionic character.

However, Waller and Lundquist (123) and Bijvoet and Lonsdale (124) have independently concluded that only at scattering angles below a certain value could the data distinguish between the two types of structure. All of the scattering angles in the available data are too high for this. Thus, it is not possible to obtain information on the bonding in lithium hydride from the available data.

5.033 Other Methods

Filler and Burstein (65), on the basis of lattice frequencies from infrared absorption, obtained a "dynamic effective ionic charge" of 0.52e. The small value as compared with the alkali halides is attributed to Li^+H^- overlap and distortion of the highly polarizable H^- .

5.04 Metallic State of LiH

The possibility of a transition of lithium hydride to a metallic form at high pressures has been considered. Griggs, McMillan, Michael, and Nas (125) studied the electrical conductivity up to 240 kilobars at room temperature, finding no effect. Behringer (126) calculated the dependence on pressure of the energy gap between the last filled band and the first empty band of LiH, and concluded that metallic lithium hydride would be produced at 35 megabars. He found that charge transfer from Li to H would affect this pressure by less than 1 megabar. However, a transition to the denser CsCl structure might lower the energy gap and produce the transition at a lower pressure.

6.00 LITHIUM DEUTERIDE AND LITHIUM TRITIDE

6.01 Comparative Properties

Only a little is known about lithium tritide, but considerable information on solid lithium deuteride is found in the literature. Table X lists the comparative properties of the hydride and deuteride. In almost all cases, the workers measuring or calculating the value tabulated for LiD used the same method as they did for LiH.

Table X
Comparative Properties of Lithium Hydride and Deuteride

	<u>LiH</u>	<u>LiD</u>	<u>References</u>	
Lattice Constant, A.	4.0834	4.0684	(45)	
Density, g/cm ³ (X-ray)	0.775	0.883	(45)	
Molar volume, cm ³ /mole (X-ray)	10.254	10.146	(45)	
Linear coefficient of expansion, °C. ⁻¹ x 10 ⁻⁵	4.2	5.7	(44) (56)	
Refractive index, n _D	1.9847	1.9856	(44)	
Melting point, °C.	688 ± 1	686 ± 5	(3) (41)	
Root-mean-square amplitude of vibration, A. (20°C.)	0.24	0.29	(52)	
Debye θ	815	611	(80)	
Zero Point Energy kcal/mole	Debye theory	1.82	1.37	(80)
	London "	1.12	0.59	(110)
	Born "	5.49	4.30	(110)
Heat of Formation, kcal/mole	-21.666	-21.784	(78)	
Lattice Energy, Born-Haber, kcal/mole	218.76	217.76	(78)	

Heumann and Salmon (98) have measured the dissociation pressures in the lithium-lithium deuteride and lithium-lithium tritide systems as a function of composition at 700°, 750°, and 800°C. Their results are shown in Table XI, along with values for the lithium-lithium hydride system measured at 700° and calculated at the higher temperatures. All values in parentheses are derived from the observed data by extrapolation or calculation.

Table XI
Plateau Results, Heumann and Salmon
Systems Li-LiH, Li-LiD, Li-LiT
 $\log p_{\text{mm}} = -A/T^\circ\text{K.} + B$

	Li-LiH	Li-LiD	Li-LiT
A	8224	7626	7325
B	9.9258	9.4836	9.2456
P _{mm} 700°C.	28	45	52
P _{mm} 750°C.	74	99	131
P _{mm} 800°C.	180	250	255
Plateau Com- 700°C.	0.26-0.96	0.28-0.94	0.31-0.91
position Lim- 750°C.	(0.30-0.94)	0.32-0.92	0.36-0.88
its Mole Fract. 800°C.	(0.35-0.92)	0.38-0.90	0.43-0.85
LiH			
t°C. for p = 1 atm.	(897)	(883)	(877)
Critical Temp. °C.	(997)	(956)	(886)

6.02 Isotope Exchange

Tronstad and Wergeland (127) (128) have carried out a series of thermodynamic estimations on lithium hydride and deuteride, using Ubbelohde's (80) zero point energy and Debye Θ values, along with known information on lithium metal, H_2 gas, and HD gas, to estimate the free energy of formation and the dissociation pressure of the hydride and deuteride up to $900^\circ K$. From these they have calculated the equilibrium constants of the following exchange reaction at a series of temperatures.

	$LiD(s) + H_2(g) + LiH(s) + HD(g)$				
$T^\circ K.$	298.1	400	500	600	700
K_p	1.34	1.65	1.7	1.8	1.9

Urey (129) has calculated the equilibrium constants of a large number of exchange reactions involving isotopic species of lithium hydride, both for lithium isotopes and hydrogen isotopes. Exchange reactions of LiH with the deuterium halides, D_2 , and D_2O are considered, from $273^\circ K$. to $600^\circ K$., by statistical mechanical methods. The exchange of LiH (solid) with Li vapor is also calculated. The calculations were for gaseous LiH molecules, but Urey has estimated that the error in applying the gas partition functions to the solid equilibria should only be about 1% in the equilibrium constant.

Table XII below shows values of the equilibrium constants for the reactions with the greatest amounts of exchange in each group.

Table XII
Exchange Reactions of Lithium Hydride and Deuteride

<u>Reaction</u>	<u>$K_{273^\circ K.}$</u>	<u>$K_{600^\circ K.}$</u>
$LiH + 1/2 D_2 = LiD + 1/2 H_2$	2.3	1.4
$Li^7D + Li^6 = Li^6D + Li^7$	1.033	1.009

Wilzbach and Kaplan (130) have measured the rate and the equilibrium constant for the exchange between lithium hydride and tritium. They found $K = 3.7$ for $(HT)(LiH)/(H_2)(LiT)$ at $200^\circ C$., as compared with 3.66 calculated by the method of Urey (129). The rate of exchange was noticeable at room temperature, and complete within 24 hours at $200^\circ C$. The kinetics were difficult to interpret, the authors suggesting a molecular diffusion process, possibly as H_3^- , as a limiting factor, This, however, seems unlikely.

Johnson (131) has described and discussed the recovery of tritium from dilute solutions of lithium tritide in lithium. Two methods are described. One is based on the crystallization of LiT at temperatures near the melting point of lithium. The other is based on sudden cooling from $700^\circ C$. to $300^\circ C$. of the vapors over the melt, with the Li metal condensing and the T_2 remaining

in the gaseous phase. The yield would depend on the relative rates of cooling and of combination of Li with T_2 .

Varshavskii and Vaisberg (132) have considered the exchange of H and D and of H and T between the alkali metal hydrides and the hydrides of nonmetals, with the largest effects for the heavier alkali hydrides.

7.00 LITHIUM HYDRIDE GAS

7.01 Introduction

When lithium metal or lithium hydride is heated in a closed tube with hydrogen above 750°C ., a characteristic absorption spectrum is noted in the violet and near ultraviolet. This spectrum, appearing only in the presence of hydrogen, has been shown to be due to the presence of gaseous LiH molecules. Some emission lines may also be found. This was first observed by Watson (133) in 1925.

Many properties of the LiH molecule and of the Li-H bond have been deduced from interpretation of the spectra, and from fundamental quantum mechanical calculations on this relatively simple diatomic molecule. The literature is so abundant that coverage in this section is not as complete as in the others.

Klemperer (134) has deduced from the intensity of the infrared emission spectrum that a considerable pressure of LiH must exist at 1400°K .--of the order of 10 mm. mercury. This would give $K = 0.005$ for the equilibrium constant of the reaction: $2 \text{Li (g)} + \text{H}_2 \text{(g)} \rightleftharpoons 2 \text{LiH (g)}$.

7.02 Spectroscopic Studies

The absorption and emission spectra of gaseous LiH were observed by Nakamura (135) (136) (137), and by Crawford and Jorgensen (138) (139) (140), who also observed the spectrum of gaseous lithium deuteride. These workers observed over 1000 lines, in 26 bands, covering the range from 3100 Å. to 4500 Å. Most of these lines could be assigned to definite quantum transitions between energy levels in the ground state ($X^1\Sigma^+$) and the first excited state ($A^1\Sigma^+$) of the molecule.

Velasco (141) observed the ultraviolet spectrum of LiH and LiD in the region from 2000-3200 Å., with a grating spectrograph of high resolving power. He discovered a new band between 2880 and 3080 Å. in each case. Continuous regions of absorption were found on the low wave length side of these bands, with absorption maxima at 2720 Å. for LiH and 2690 Å. for LiD. This band was attributed to the second higher electronic level ($B^1\Pi$). Rotational and vibrational analyses were made.

Klemperer (134) observed the infrared emission spectrum of LiH up to 1400°K. in the region from 970 cm^{-1} to 1500 cm^{-1} .

7.03 Molecular Properties of LiH and LiD

Some of the more significant properties of these molecules are listed in Table XIII. Most of the values given are derived from the work of Velasco (141), or of Crawford and Jorgensen (138) (139) (140) as reported by Herzberg (142).

The dipole moment of 6.0 Debyes is based upon a series of six reported values (143) (144) (145) (146) (147) (148). The older reported values of 3.5-4.05 D (149) (150) seem to be definitely excluded by the clustering of so many recent calculations about the value of 6.0.

The total binding energy is that calculated from experimental data by Miller, Friedman, Hurst, and Matsen (153). It represents the energy of formation of the LiH molecule from Li and H nuclei plus electrons.

Table XIII
Properties of Lithium Hydride and Lithium Deuteride Gas Molecules

	<u>State</u>	<u>LiH</u>	<u>LiD</u>
Equilibrium Internuclear Distance, A.U.	Ground	1.5953(142)	1.5949 (142)
	1st. excited	2.596 (142)	2.586 (142)
	2nd excited	2.378 (141)	2.376 (141)
Dissociation Energy, Electron volts (Normal atoms)	Ground	2.5154(141)	2.5160 (141)
	1st. excited	1.0765(141)	1.0770 (141)
	2nd excited	0.035 (141)	0.036 (141)
Vibration Freq., Li^7 molecule, cm^{-1}		1405.65(129)	1055.12(129)
Vibration Freq., Li^6 molecule, cm^{-1}		1420.32(129)	1074.59(129)
Dipole Moment, Debyes		6.0 $\pm$ 0.6*	
Total binding energy, electron volts		219.71(153)	

* (143) (144) (145) (146) (147) (148)

7.04 Thermodynamic Properties of LiH Gas

Certain thermodynamic properties of the LiH molecule at 298°K. have been calculated, and are tabulated in the "Selected Properties" of the National Bureau of Standards (151). These are:

Heat of Formation	$\Delta H^\circ = + 30.7 \text{ kcal/mole}$
Entropy	$S^\circ = 40.77 \text{ e.u.}$
Free Energy of Formation	$\Delta F^\circ = + 25.2 \text{ kcal/mole}$
Heat Capacity	$C_p^\circ = 7.06 \text{ cal/mole-deg.}$

These enable the calculation of the heat of sublimation and the free energy of sublimation of solid LiH into gaseous LiH:

$$\text{LiH (s)} = \text{LiH (g)} , \Delta H^\circ = +52.0 \text{ kcal}; \Delta F^\circ = +41.7 \text{ kcal.}$$

The heat of sublimation should not be very different at high temperatures, but the free energy of sublimation will undoubtedly be less positive at higher temperatures, corresponding to increasing relative stability of LiH (g). It is improbable, however, that the actual concentration of LiH gas will be significant at temperatures at which solid LiH is stable at 1 atm. pressure. This concentration should be susceptible to calculation by statistical mechanical methods from the spectral data.

Krieger (152), in a report evaluating solid lithium hydride as a rocket propellant, calculated molecular weights, enthalpies in cal/gram, and entropies in cal/gram-deg., for equilibrium gas mixtures of the overall composition LiH at various temperatures and pressures, but did not report the equilibrium concentrations of the individual species.

7.05 Quantum Mechanical Studies

A very large number of theoretical investigations of the lithium hydride molecule have been made. The following is a partial list of papers on quantum mechanical calculations on the lithium hydride molecule: Hutchisson and Muskat, 1932 (154), Knipp, 1936 (155); Mulliken, 1936 (156); Mueller and Eyring, 1951 (157); Fischer, 1951-3 (158) (159) (160); Klemperer and Margrave, 1952 (150); Hurley, 1954 (161) and 1958 (143); Karo, 1958-9 (144) (162) (163), and Matsen and co-workers (145) (146) (147) (148) (153) (164) (165).

Dissociation energies, binding energies, interatomic distances, dipole moments, and electron density distributions were calculated, and compared with experimental values where available. In general the various methods do not give agreement with experiment in both energy and distance.

Several workers calculated values very close to 217 e.v. (146) (148) (153) (166) for the binding energy, although the experimental value is reported as 219.71 (153).

Hurley (161) gives the following equation for the Morse curve of the LiH molecule in the ground state from spectroscopic data:

$$U(r) = 0.096 [1 - e^{-0.586(R-3.02)^2}]$$

Hurley (161) and Karo and Olsen (144) calculated theoretical Morse curves.

Hurley (143) assigns 41% ionic character to the Li-H bond in gaseous LiH.

8.00 CHEMICAL PROPERTIES

8.01 Introduction

The chemical behavior is only qualitatively similar to that of the other saline hydrides. It most resembles calcium hydride in its reactivity with inorganic materials, air, water, etc., but is considerably more covalent in nature, which aids in interpreting its differences from calcium and other binary saline hydrides. Thus, it is a less vigorous reducing agent than calcium hydride in metallurgical reactions, but more vigorous in organic reductions where its covalent nature is important. Hurd (6) suggests a vestigial solubility in ethers which, if true, helps to explain the greater reactivity of lithium hydride with organic reactants in anhydrous solvents.

The reactivity of lithium hydride above red heat is similar to that of lithium metal which, of course, it forms by endothermic dissociation. The free energy of formation of lithium hydride approaches zero at about 800-900° C. Thus, its reactions become similar, thermodynamically, to those of lithium. The heat of formation, however, is still considerable at this temperature; hence, the reactions are usually less vigorous than those of lithium. The heat of reaction of: $MO + 2Li = Li_2O + M$ is greater than that of: $MO + 2LiH = Li_2O + M + H_2$ by the heat of the reaction: $2LiH = 2Li + H_2$. As noted above, the latter heat is quite significant, being endothermic by 44 kcal. at room temperature and by somewhat less than this for metallurgical temperatures. Lithium hydride may therefore react (in the practical sense) only incompletely with oxides, halides, etc. which are rapidly reduced by lithium metal. The heat of formation of Li_2O is about 10 kcal. less than that of CaO , and accordingly it might be expected that lithium is a less powerful reducing agent than calcium. This is also true of the hydrides despite the higher heat of formation of calcium hydride.

The reaction of lithium hydride with water and alcohols provides molecular hydrogen rather than atomic or "nascent" hydrogen. For this reason, it is a much less powerful reducing agent than lithium when dropped into water, alcohols, etc., containing reducible solutes. This is true of all the binary saline hydrides. The reducing action is similarly less than that of lithium towards organic reactants such as esters. The insolubility, high lattice

energy (218 kcal.), and stability of lithium hydride render it incapable of exhibiting the high reduction potential of the hydride ion ($E^\circ_{298} = -2.2$ volts for $1/2 \text{ H}_2 + e^- = \text{H}^-$) shown by e.g. aluminum hydride and lithium aluminum hydride in their organic reactions.

8.02 Reaction of Lithium Hydride with Water and Air

The finely powdered hydride reacts rapidly with air of low humidity, forming LiOH , Li_2O , and Li_2CO_3 . In moist air the powder may ignite spontaneously, when it burns fiercely, forming a mixture of products including some nitrogenous compounds. The lump material reacts with humid air forming a superficial coating which is a viscous fluid. This inhibits further reaction, and several hours' exposure of a one-inch cube does not cause appreciable loss of hydrogen therefrom, although the appearance of a film of "tarnish" is quite evident. Little or no nitride is formed on exposure to humid air. The lump material, contained in a metal dish, may be heated in air to slightly below 200°C . without igniting, although it ignites readily when touched by an open flame. The condition of the hydride surface, presence of oxides on the metal dish, etc., have a considerable effect on the ignition temperature. Perfectly dry oxygen does not react with crystalline LiH unless heated strongly, when an almost explosive combustion occurs.

Both the powder and lump material generally ignite when moistened, the former sometimes giving a dust-explosion of some violence. Air-free steam reacts rather more slowly than might be expected, owing to the protective film which forms on the hydride.

Much work has been done on the rate of reaction of water with lithium hydride. This is contained in unavailable Chemical Corps, Signal Corps, and Navy reports issued during the war. The rate studies are very complicated due to the difficulties of reproducing the active surface area, mixing, temperature, pH, etc. The typical one-pound charge of lump hydride used in field generators produced 7 to 10 cu. ft. hydrogen per minute.

The reaction with water appears to give lithium hydroxide at ordinary temperatures and possibly lithium oxide at higher temperatures by analogy with calcium hydride, which above 400°C . yields CaO rather than Ca(OH)_2 (167).

8.03 Reactions with Acidic Substances

Reactions leading to the formation of hydrides of metals or metalloids are separately discussed in Section 8.07.

Lithium hydride reacts more rapidly with aqueous solutions of acids than with water. In the presence of traces of moisture, it reacts slowly with carbon dioxide at room temperature, forming the carbonate. Hydrogen sulfide similarly yields lithium sulfide, etc.

In the absence of moisture, the hydride reacts with surprising reluctance with HCl and Cl₂ gases, a temperature of 500°C. being required to complete the reaction. With sulfur dioxide, the following reaction occurs: (9)

Above 50°C. the sulfide is formed. With dry carbon dioxide, the following reactions were reported by Moissan (9):

Silicon dioxide reacts readily at red heat giving a brown glassy material presumably containing silicon or "silicon monoxide" (168) and possibly lithium silicate. Lithium hydride shares with lithium the ability to crack glass, Vycor, or quartz on contact at temperatures only slightly above 180°C. For this reason glass or quartz or enamelled containers should never be used.

Anhydrous organic acids, phenols, acid anhydrides react slowly with lithium hydride, for the most part, giving hydrogen gas and the lithium salt of the acid.

Lithium hydride reacts with acetylene to form lithium carbide and hydrogen (9).

8.04 Reactions with Basic Substances

Ammonia reacts very slowly with lithium hydride at room temperature or below, but rapidly above 300°C., yielding the amide LiNH₂ quantitatively (9). The presumed analogous reactions with primary and secondary amines have not been studied. Tertiary amines are not reactive at ordinary temperatures.

Alkali metal oxides are presumed to exist in equilibrium with lithium hydride in the molten state, e.g.:

This should also be the case for calcium group metal oxides. The reactions have not been studied, but since LiH is more stable than other alkali metal hydrides, the above-mentioned reaction should go to completion at temperatures where MH is largely dissociated. Continuous removal of hydrogen should force this reaction to go to virtual completion, viz:

The lithium oxide may coexist with lithium hydride, no water being formed.

Lithium hydroxide reacts irreversibly with lithium hydride, forming the oxide and hydrogen:

This reaction sets in on heating at about 300-350°C., which could very well be the temperature of the LiH-LiOH eutectic. It seems likely that other hydroxides act similarly, although sodium hydroxide fails to react with sodium hydride and rather forms a solution (169). There is also a possibility of metathesis followed by the reaction of lithium hydride with the lithium hydroxide formed.

Frazer (170) reported the following reaction with Li_2CO_3 :

The reaction occurs in a solid compact at 350°-400°C. H_2 and CO_2 are also formed to a certain extent, but may be separated from the methane by cold trapping. Since the methane produced has little or no gaseous impurity, and since all of the H is from one source, Frazer patented the use of the reaction to produce methane in which only one definite isotopic species of C and one of H is present.

8.05 Reactions of LiH with Miscellaneous Inorganic Substances

The complex series of reactions between lithium hydride and nitrogen gas was investigated by Dafert and Miklauz (10) (11) (171). (This set of reactions is closely related to those between Li_3N and H_2 .) Reaction began at 160°C., and became rapid at 200°-250°. Li_3NH_4 was reported to be formed here (10), decomposing to Li_3NH_2 on further heating to 340°, and to lithium imide, Li_2NH , on heating to 600°-800°C. The imide may be formed directly on heating lithium hydride with nitrogen to these temperatures:

Ruff and Goerges (172) disputed Dafert and Miklauz's interpretations of these reactions, postulating no intermediates other than Li_2NH and LiNH_2 , but Dafert and Miklauz (35) defended their postulation of the "trilithium amide".

Carbon was reported by Peters (14) to react with lithium hydride, to form lithium carbide, but the reaction has not been well studied. Hydrogen and possibly methane are also formed. Massive graphite, which is commonly used in the electrolytic cells in which lithium is prepared, is only slightly attacked by the hydride. Carbide or graphite inclusions in metals are thought to react with molten hydride, but this has not been unequivocally established.

Moissan (9) found the following reactions with carbon monoxide and with cyanogen:

The older literature cites a reaction with lithium chloride at red heat yielding a "subchloride" (173), which was later shown to be an equimolar mixture of LiH and LiCl (174). The alkali metal chlorides are reduced in part, at red heat, owing to removal of the volatile components, metal and hydrogen (168). Molten systems containing, for example, Na, Li, H, LiCl, and NaCl are presumably formed first. Magnesium chloride is probably first reduced to magnesium hydride, which then decomposes. Palladium chloride reacts almost explosively. Metals which form hydrides stable at red heat (Ti, Zr, Ta) may yield hydrides via these reactions.

The reductions by oxides and chlorides are analogous:

Pearce, Burns, and Ganz (168) studied the reaction of LiH with a series of transition metal oxides. TiO_2 was reduced to Ti_2O_3 , ZrO_2 to Zr (some ZrO , Zr_2O_3 ?), and GeO_2 to GeO (some Ge), in the solid state at 600°C . ThO_2 was not reduced by LiH. V_2O_5 was reduced to VO , Nb_2O_5 to Nb_2O_3 , and Ta_2O_5 to TaO_2 , by LiH in fused LiCl-KCl eutectic at 350°C .

Mercury reacts slowly with lithium hydride forming an amalgam and evolving hydrogen. This reaction is probably general for low melting metals which do not form stable hydrides and which do form metallic compounds with lithium (e.g., Tl, Sn, Pb, Sb, Bi).

Powdered magnesium reacts with calcium hydride on heating, presumably by forming unstable MgH_2 which decomposes as rapidly as it is formed, at dull red heat. It is possible that this reaction also occurs with lithium hydride. No evidence exists for an analogous reaction between massive iron or nickel and lithium hydride at or below 800°C .

The electrolysis of LiH is discussed in Section 2.031.

8.06 Reactions of LiH with Miscellaneous Organic Substances

Lithium hydride is a poor reducing agent and seems to act more like a strongly basic reagent. Thus, it is a powerful condensing agent for aldol and Claisen condensations in the same sense as sodium alcoholates:

It may, under rigorous conditions, react with labile halogen atoms, especially iodine, to form lithium halide. In general, such reactions are feasible only in the presence of aluminum chloride or lithium aluminum hydride. Carson and Carter (175) have used the smoothness of the reaction: $RI + LiH = RH + LiI$ in ether in the presence of dissolved $LiAlH_4$ to determine the heats of formation of the organic iodides.

It effects the reduction of acid chlorides ($RCOCl$) or thioesters ($RCOSR'$) to the aldehydes ($RCHO$), on boiling in benzene, toluene, or xylene (176). With benzyl chloride at $150-210^\circ C.$, benzoyl benzoate is formed, with traces of benzaldehyde (177). It was shown that LiH catalyzed the condensation of two molecules of benzaldehyde to benzyl benzoate.

Phthalocyanine reacts with lithium hydride, yielding lithium phthalocyanine (178).

Lithium hydride reacts vigorously with lower alcohols, and slowly with higher alcohols and phenols. It reacts with carboxylic, sulfonic, etc. acids, forming salts. Lithium hydride is therefore not generally compatible with plastics containing hydroxyl, aldehyde, ketone, acid, or ester groups. Its long-term reaction with anhydride, amide, nitro, and possibly nitrile groups may be suspected. Thus, only hydrocarbons or ethers are definitely known to be inert. The compatibility of hydrides with rubbers, etc. has been studied to some extent (229). Presumably no reaction occurs with silicone rubbers, but this has not been established experimentally.

Gotman (179) has reduced polyvinyl chloride with LiH in boiling tetrahydrofuran containing some $LiAlH_4$, to yield a polyhydrocarbon similar to polyethylene. Some atmospheric oxygen is incorporated into the polymer as OH groups.

8.07 Reactions of LiH Leading to Hydrides of Metals and Metalloids

The most significant of these is the well-known reaction of LiH with aluminum chloride in diethyl ether under anaerobic conditions to form lithium aluminum hydride, $LiAlH_4$, as first reported by Finholt, Bond, and Schlesinger (180):

The lithium chloride, insoluble in ether, is filtered off.

The $LiAlH_4$ produced is a more versatile agent for hydride synthesis than LiH . This report is confined to syntheses effected by lithium hydride.

Mikheeva, Fedneva, and Shnitkova (181) have studied the conditions for optimum yields in this reaction. Wiberg, Bauer, Schmidt, and Uson (182) have reported the use of iodine to initiate this reaction.

A change in the conditions of the reaction leads to the formation instead of polymeric, ether solvated aluminum hydride, $(AlH_3)_x$ (180):

Diborane, B_2H_6 , may be synthesized from lithium hydride and boron trifluoride in ether solution: (183) (184) (185) (186)

The following reaction is also reported: (183) (186)

Hurd (187) reports a general reduction of gaseous boron halides to diborane above $200^\circ C.$, and evidence for diborane formation in the explosive reaction of lithium hydride with powdered B_2O_3 .

Lithium borohydride, $LiBH_4$, may be prepared from lithium hydride and diborane in ether solution: (186) (188)

It may also be prepared from lithium hydride and $B(OCH_3)_3$ (189).

The formation of several substituted borohydrides by addition of lithium hydride to boron compounds has been reported:

It is probable that many reactions of LiH involve this kind of addition as a first step.

Aluminum ethoxide reacts with lithium hydride in ether to give $(Et_2O)_2 \cdot AlH_2Li$, and finally $LiAlH_4$ (192). With $Et_2AlCl \cdot Et_2O$, LiH in ether suspension yields Et_2AlH in ether solution (29).

Finholt, Bond, Wilzbach, and Schlesinger (193) prepared diethyl silane from the reduction of diethyl dichlorosilane with LiH , but found that in general LiH was poorer than $LiAlH_4$ for reduction of silanes:

However, Ponomarenko and Mironov (27) were able to reduce several chlorosilanes to silanes by long refluxing in isoamyl ether.

Wiberg and Bauer (194) have reported the preparation of MgH_2 from LiH and $MgBr_2$, and also of polymeric beryllium hydride, $(BeH_2)_x$ from LiH and $BeCl_2$, both preparations in ether solution. The second synthesis is also reported elsewhere (195).

Wiberg and coworkers have also reported the syntheses of additional hydrides from reactions of lithium hydride with metal halides in ether solution: LiGaH_4 (196), also reported by Finholt, Bond, and Schlesinger (180), $(\text{InH}_3)_x$ (197), $\text{LiInBr}_3 \cdot 6\text{Et}_2\text{O}$ and $\text{LiInI}_3 \cdot 6\text{Et}_2\text{O}$ (198), ZnH_2 and ZnHI from ZnI_2 (199), and SbH_3 from SbCl_5 (200). A hydride of Tl could not be synthesized from TlCl_3 and LiH (201).

9.00 OTHER CONSIDERATIONS ON LITHIUM HYDRIDE

9.01 Miscellaneous Applications.

Lithium hydride may be used as a catalyst for many organic reactions, chiefly polymerizations. In many cases, other hydrides such as NaH or CaH_2 , will also be effective.

Synthetic rubbers have been made by the polymerization of diolefins using lithium hydride as a catalyst (202). Lithium hydride is also used as a catalyst to effect the synthesis of glycol terephthalates (203) (204), and to effect the polymerization of ϵ -caprolactam (205).

Field and Feller (206) (207) (208) have patented the use of combinations of lithium hydride with oxides such as NiO , V_2O_5 , and MoO_3 , as catalysts in the polymerization of ethylene. Volts (209) has also studied the use of unsupported LiH as a catalyst in the formation of polyethylene.

LiH will catalyze the reaction of 1,3 butadiene with NH_3 to form amines (210), the reaction of a glycol with phosphate and phosphite esters (211), and the side chain ethylation of toluene (209) (212):

The use of LiH as a hydrogen storage medium for balloons (22) and for fuel cells (23) has been cited. Its use as a rocket fuel has been proposed and investigated (152) (213).

Other miscellaneous applications are: its use in ether solutions of AlCl_3 to provide the electrolyte for electrodeposition of aluminum (214) (215), its use as a desulfurizing agent in iron and steel (216), and its use in making certain metal foams (217). In the last case, LiH is ground in molten metals such as Li , Mg , and their alloys, and quickly cooled to the solid state before the dissipation of the foam.

9.02 Corrosive Character of Molten Lithium Hydride

This matter has not been adequately investigated and results of various workers seldom agree. Probably, the reason for this lack of agreement lies in the considerable effect of impurities present in the hydride and of the cleanliness of the containers whose resistance is being ascertained. Moreover, the effect of even brief exposure of the hydride or container to air has sometimes been neglected.

Molten lithium hydride of high purity does not appear to attack Armco iron, 312 or 347 stainless steels at temperatures below 720°C. Vessels made from these materials have been used repeatedly in this laboratory and elsewhere without evidence of corrosion. A 347-alloy bomb contained molten lithium hydride for 150 hours at temperatures up to 1050°C. and showed, on metallographic examination, a roughened surface layer only 0.01 mm thick. (97)

The hydride showed a spectrographic trace of nickel but no chromium or iron. The latter may have been overlooked, however, owing to the very small amounts present.

The presence of impurities, including those due to exposure of lithium hydride to air, may profoundly affect the corrosive character. Lithium oxide and lithium chloride are extremely corrosive to most metals and ceramics. The former is a common result of undue exposure to air; the latter is present in most commercial lithium in varying amounts. The corrosive properties of other likely impurities have not been ascertained.

Vessels in which the hydride is to be melted should be scrupulously cleaned and pretreated with molten hydride and hydrogen. (see paragraph (1.04)) Anaerobic technique is recommended for handling the hydride and the cleaned container. If the container is welded, special attention should be given to ensuring absence of pockets of flux. Atomic hydrogen welds are recommended. Neither mild steel nor silica are recommended for containers, despite favorable experience of others reported for molten lithium. (218)

The tendency of lithium to alloy with various metals is discussed in the "liquid Metals Handbook" and in the older literature. (219)

9.03 Handling and Fabrication of Lithium Hydride

If the hydride is to be heated or stored in an hermetical, full container, it is imperative that no gas shall be evolved irreversibly. This is readily ensured by 100% anaerobic handling of the hydride from the time it is prepared. For large scale operations, where a mass of large crystals is obtained from the preparation, these may be transferred in dry air to a nitrogen drybox without serious contamination. All crushing and grinding operations should be carried out in dry nitrogen, argon, or helium and the crushed or powdered product not thereafter exposed to air.

Lithium hydride dust is apt to explode in humid air or, even in dry air, due to static electricity. Moreover, it is extremely irritating to the mucous membranes and skin, causing an allergic skin reaction in some individuals. Lithium salts are sometimes toxic. Drybox handling eliminates these hazards.

The hydride must not be moistened or exposed to an open flame. Burning hydride is best extinguished by smothering with an inverted can or pail, or by covering with bone dry graphite powder or dolomite. Carbon dioxide, carbon

tetrachloride, or aqueous fire extinguishers, must not be used since an explosion may result. Sand may react explosively with burning hydride, especially if sand is not completely dry, or contains hygroscopic sea salt.

Powdered lithium hydride is easily formed into pellets of theoretical density by powder-metallurgy techniques. No binder is used. The dry powder is loaded anaerobically into the clean die and compressed at 20 T.SI. or more. Most of the writer's experience was with a 1/2" carbolloy cylindrical die, but no difficulty was encountered with a 1.8" tool steel die (Airkool Steel Rockwell 65), or with a home-made steel press-plate which made 1/2" square bars. The pressings are conveniently carried out by loading the die in a drybox and extruding the pellet into a jar containing argon and held by a rubber flange on to the base of the die. The pressing characteristics resemble those of dry sodium chloride and very hard pellets may be obtained. In the event that the die is not highly polished, it may be necessary to wipe the walls with a suspension of colloidal graphite (DAG 154) in acetone, and then dry thoroughly. Very little graphite wipes off on the pellets if this is done properly. The pressed shapes may be sawed (in the drybox) and resemble, in hardness and glossy appearance, the common white "life saver" candies.

Schell, Taub, and Doll (220) have thoroughly investigated the hot pressing of lithium hydride. Their recommended temperature range was 600°-620°C., with pressures of 1000-1500 psi. Densities of the compacts were 98% or better of theoretical.

It was necessary to use these high temperatures and pressures to achieve this. The dies were of iron-plated graphite, an Aquadag coating being used on the iron-graphite surface. All manipulations - rolling, ball milling, pressing - were carried out in a helium drybox on a continuous basis.

Lithium hydride may also be cast into shapes. This operation is rendered difficult by the unusually large shrinkage when the melt solidifies. This has been estimated as 16% (5). The solidifying melt shrinks from the center leaving usually a funnel-shaped indentation. The edges of the top meniscus are drawn down sharply from the walls towards the center and some cracking may occur. The lower parts of the casting are usually sound, at least in small molds where the thermal gradients are not large. In any event, the thermal gradient should be such that the bottom cools first. The cooled polycrystalline product adheres tenaciously to the mold but the material is sufficiently brittle so that tapping the mold often frees the casting. The authors have no data on the bulk density of castings, but it is likely that fissures, voids and lattice imperfections will reduce this to a small extent.

Lithium hydride dust is apt to explode in humid air due presumably to local heating of particles by reaction with moisture. It is also possible for explosions to occur in transferring lithium hydride in fine powder form in dry air, presumably due to static electricity.

A study of the inhalation toxicity of lithium hydride has been made by Spiegl et al (221). All effects seem to be those due to alkalinity.

9.04 Properties of Containers of Lithium Hydride

The reactivity of the hydride with air makes necessary an air-tight moisture-proof container. If the container is to be heated, it must also be impermeable to the hydrogen produced by thermal dissociation of the hydride. Several types of plastic containers (aluminum foil-lined) and ceramics are generally suitable for room temperature use but metals are preferred at higher temperatures. Stainless steels 316 and 347 have a combination of hydrogen impermeability and hot strength which suggests their use for containers.

Owing to the fact that stoichiometric LiH exhibits a higher thermal dissociation pressure than compositions containing slightly less hydrogen, and since the decrease in hydrogen content may be offset by the attendant decrease in necessary container thickness; it follows, that there will be an optimum composition containing somewhat less than the stoichiometric amount of hydrogen which, when loaded into a minimum weight shell, will give the maximum over-all N_H at a given temperature. This composition and shell-thickness may be evaluated for cylindrical containers using the A.S.M.E. code formula for maximum safe working pressures and the data on density and dissociation pressure for lithium hydride cited earlier. The rapid decline in tensile strength with temperature of container materials must be taken into account. This calculation yields an optimum design of container and system which may be scaled up in size until the walls become thick enough to prevent diffusion loss at operating temperatures, as well as to safeguard against superficial flaws in the metal.

The relatively great thermal stability of lithium hydride implies that the container may be very light and that the N_H of hydride-plus-container should be only slightly less than for unclad hydride up to approximately 800°C. Hydrogen diffusion loss through stainless steels according to Gibb and McSharry (97) is given below.

<u>Alloy</u>	<u>Temperature</u>	<u>Pressure</u>	<u>cc/cm²/mm/hr.</u>
316	650°C	1 atm.	0.009 to 0.03
347	650°C	1 atm.	0.01 to 0.04
304	650°C	1 atm.	0.003 to 0.04

For molybdenum, the diffusion loss at 650°C. and 1 atm. is calculated to be of the order of 4×10^{-12} cc/cm²/mm/hr. although it is doubtful if the commercial sintered metal would show the theoretical permeability.

9.05 Analysis of Lithium Hydride.

The material is commonly assayed by measuring the volume of hydrogen evolved by hydrolysis. This is best performed with a sufficiently large apparatus to permit samples weighing a gram or more to be used. The best technique is to allow the evolved hydrogen to displace water contained in a large flask kept at a constant head of pressure. The displaced water is allowed to

flow into a beaker which is weighed on a platform balance. The evolution flask should contain nitrogen or argon, not only to prevent premature hydrolysis by moist air, but also to prevent an explosive reaction. The latter may be moderated by adding purified dry dioxane before adding water to the sample.

Hydrogen has also been determined in LiH by using a metal which readily alloys with lithium to decompose the hydride. Bergstrasser and Waterbury (222) have decomposed the hydride with lead at 600° C., the evolved hydrogen being oxidized to water by CuO, and the water absorbed and weighed. Frazer, Schoenfelder, and Tromp (223) have decomposed lithium hydride with boiling mercury and measured the evolved hydrogen.

Total lithium may be determined by various methods (224) (225) but in view of the precision of the determination of total hydrogen by evolution, lithium determination does not appear to be too useful. The difference between total hydride by evolution and total base by titration of the hydrolysis residue permits a rough calculation to be made of Li metal and LiH contents, but this is subject to obvious errors if a correction is not made for other bases present.

If it is assumed that the only substances present are Li, LiH, and Li₂O, a useful approximation of the relative "contents" of the three components may be made by the solution of these three simultaneous equations:

$$(\text{Wt. LiH}/7.94) + (\text{Wt. Li}/6.94) + (\text{Wt. Li}_2\text{O}/14.94) = \text{moles base}$$

$$(\text{Wt. LiH}/7.94) + (\text{Wt. Li}/13.88) = (\text{Volume H}_2 \text{ S.T.P.})/22,400$$

$$\text{Wt. LiH} + \text{Wt. Li} + \text{Wt. Li}_2\text{O} = \text{Wt. sample}$$

A similar set of equations could be derived assuming the basic impurity to be LiOH. A sample contaminated by air at room temperature would probably contain both LiOH and Li₂O, and a simple titration could not distinguish between these. A sample which had been heated above 300° C. and protected from air contamination thereafter would contain only Li₂O.

Lithium hydroxide has been independently determined by Friedman (226), by reacting the sample in methanol with benzoic acid, followed by a titration with Karl Fischer reagent. The Li₂CO₃ content must be known and corrected for, since this substance also reacts with benzoic acid. Frazer, Schoenfelder, and Tromp (223) have determined LiOH from the measurement of the hydrogen evolved on heating by the reaction: LiOH + LiH = Li₂O + H₂.

Lithium oxide could presumably be independently determined by a method used for pxide in lithium (218), namely dissolving in absolute ethyl alcohol and filtering off the insoluble oxide, which is then determined by titration with standard acid. The nitride usually present must be determined and subtracted off.

Lithium Carbonate was determined (227) by hydrolysis of the sample (presumably the aqueous residue from hydrolysis) in constant boiling HCl, the evolved CO_2 being measured as a gas. Li_2CO_3 can also be determined (assuming only Li_2CO_3 , Li_2O , and LiOH in the hydrolysis residue) from the difference between the titration of the basic solution with standard acid to the bromthymol blue (pH 7) end point and the methyl orange (pH 4) end point.

Nitrogen is determined by Kjeldahl distillation, the solid hydride being placed in the distillation flask to which ice water is added anaerobically through the condenser. The mixture is kept as cold as possible until the reaction abates. A very brief boiling completes the transfer of ammonia to the condensate. Due precaution to avoid carry-over of alkaline spray must be taken even to the extent of redistilling after addition of sodium hydroxide. The mixed indicator mannitol-boric acid method is recommended.

Carbon as carbide is determined colorimetrically by passing hydrogen evolved by hydrolysis into ammoniacal cuprous chloride solution with gum arabic as a stabilizer. The red cuprous acetylide suspension is determined in a photoelectric photometer. Careful standardization is necessary.

Total carbon has been determined by combustion, but this is not recommended. The entire silica combustion tube must be protected from Li_2O smoke by a liner of stainless steel foil.

Chloride is best determined in the aqueous residue from hydrolysis by addition of nitric acid, filtration (use a weighed medium sinter) and precipitation with silver nitrate. This procedure is not entirely reliable, owing to the high concentration of lithium ions. Distillation of the acidified solution might be preferable but has not been thoroughly studied.

The acid-insolubles are dried on the above-mentioned sintered filter and weighed. Fragments of graphite are occasionally noted.

No simple chemical procedure has been developed for sodium and potassium. The amounts vary widely in the commercial hydride from a few parts per million to 1% or more. The spectrographic technique of Owen (228) is probably the best method, although flame photometry appears promising. The spectrographic technique has the advantage that it also reveals the presence of trace impurities such as iron, nickel, chromium, magnesium, boron, etc.

Friedman (226) has worked out techniques for the determination of various elements in lithium hydride, lithium hydroxide, or lithium metal. The above reference lists the reports in which full details are given for the following procedures:

Iron is determined photometrically, with o-phenanthroline at a controlled pH. If the amount is small, zirconium hydroxide may be needed as a carrier.

Nickel is determined with dimethylglyoxime.

Copper is determined with diethylthiocarbamate following removal of the nickel.

Chromium is determined with diphenylcarbazide, following precipitation on $\text{Al}(\text{OH})_3$ as a carrier.

Aluminum is determined colorimetrically with "aluminum reagent". Li^+ must be present in the standard in the same concentration as in the sample.

Silicon is determined by a procedure based on the ammonium molybdate method.

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