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A SURVEY REPORT ON LITHIUM HYDRIDE

By
Thomas R. P. Gibb, Jr.
C. E. Messer

May 2, 1954

Department of Chemistry
Tufts College
Medford, Massachusetts

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A SURVEY REPORT ON LITHIUM HYDRIDE

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SUMMARY

The physical and chemical properties of ^{LiH}lithium hydride are described based on available unclassified literature and on the author's own data. The history, preparation, thermal dissociation, corrosive character, utilization, analysis, handling and fabrication are discussed briefly. Some elementary considerations on the properties of containers are presented. Lithium deuteride is compared with the hydride. Consideration is given to practical matters as well as to theory. Where possible, data from the literature is presented critically. 90 Reference

This summary-report is written from the chemical point of view, and while it relates to the possible use of LiH for shielding, no nuclear data are included. Several recent summaries of nuclear properties are available and this laboratory is not qualified to handle such aspects of the subject.

The properties of LiH which bear particularly on the shielding problem are: thermal dissociation and recombination; irradiation-induced decomposition; chemical reaction with air, moisture, impurities; corrosion of containers; compressibility and density; melting behavior; engineering and practical considerations such as handling, fire hazards, toxicity, compatibility, analysis, etc.

These topics are considered explicitly or by obvious implication in the following pages. Part of the information presented is from the recent literature and while a critical selection has been made in some cases, it is not always possible to judge the reliability of the data reviewed. While the half-dozen values of the density of LiH have been resolved by our own measurements, it has not been feasible for us to examine all of the conflicting data in this way. We have ventured a few predictions when we believed these might be helpful to fill in needed areas where information is lacking. These are not rigorous and should be carefully differentiated from the results of actual experiments.

We have included thermodynamic properties in the belief that these will permit calculation of needed engineering data. Our current research efforts are directed in part towards adding to the list of such properties.

1.00 General Considerations on LiH

Lithium hydride has an N_H of 5.90 compared to 6.68 for water at room temperature. It may, however, be heated to red heat in a thin-wall container without requiring a pressure shell, and appears to be stable indefinitely at this temperature. Its radiation stability is evidently great (1) it may be fabricated easily by melting or compression in an inert atmosphere. 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, thus the presence of impurities affects its thermal stability in a sealed container and its corrosive character.

1.01 Classification 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 at ca. 700°C it forms as a fluid melt which crystallizes on cooling below the melting point (680°C). By employing pure lithium and hydrogen and a scrupulously cleaned container a mass of large colorless cubes may be formed on slow cooling. Preparation of single crystals by the Stockbarger or Kyropoulos technique has not been generally successful but there seems no reason why such crystals could not be grown by special techniques. The tendency to crystallize is well marked. As ordinarily prepared it may be gray and translucent or brownish and opaque, resembling calcium carbide. Coloration is due to impurities or to incomplete absorption of hydrogen. The white crystals are photosensitive and turn orange-brown on prolonged exposure to diffuse light. It is possible that traces of impurity or lattice defects promote this property which, however, is common to other saline hydrides and halides (e.g. rocksalt).

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: $\text{LiOH} + \text{LiH} = \text{Li}_2\text{O} + \text{H}_2$.

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 result 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 negligibly small below dull red heat. The relation of pressure to temperature and hydrogen-content is discussed in a subsequent section. Lithium hydride is one of the few saline hydrides which melts (see above) and melting is accompanied by a considerable contraction in volume. The melt is probably not as corrosive as has been believed, since pure hydride may be melted repeatedly in especially cleaned iron and stainless steel containers without apparent attack. The presence of impurities, air, carbides, etc. is probably detrimental.

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.

Owing to the high heat of formation of LiH it is a less powerful reducing agent in the metallurgical sense than Li metal. It does effect the reduction of many metal oxides at or above dull red heat, the slightly volatile and extremely corrosive Li_2O being formed.

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 such carbides and halides. There appears to be no inert liquid solvent although vestigial solubility in glycol ethers has been reported (loc cit). The hydride may be dispersed in most hydrocarbons, ethers, unreactive alkyl halides, esters (no 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

Lithium hydride was probably first prepared by Hautfeuille and Troost (2) in 1874 by synthesis from the elements. Their product was impure, corresponding to roughly 50% hydride or Li_2H which is not surprising in view of the fact that lithium metal had been prepared, after many failures, only 19 years before and was not available in pure form. In 1900 Matignon succeeded in forcing even less hydrogen into lithium obtaining a composition of approximately Li_3H . The stoichiometric or at least nearly stoichiometric material was prepared by Guntz in 1896 (3) and by various workers since that time. Large variations in analysis have been reported 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 (4) who noted that the hydrogen had evidently acquired an electron making it analogous to a halide ion. Moers (5) and subsequently Peters and Bardwell showed that electrolysis of molten lithium hydride resulted in hydrogen evolution at the anode. The melting point of LiH was observed by Dafert and Miklausz (6) to be 680°C . This was corroborated by K. Moers (loc cit). Gibb et al observed a melting point of 680°C which is probably not more than 2° below the correct value. (7)

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

Gmelin "Handbuch der anorganische chemie" 8th ed. et seq. Verlag Chemie, Berlin 1927 Main Vol. 20 p 71.

Sidgwick "The Chemical Elements and their Compounds" Oxford Press, 1950 Vol. I pp 21, 66

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

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

Hurd "Chemistry of the Hydrides" John Wiley and Sons, Inc. N.Y. 1952 p.27

Emeleus and Anderson "Modern Aspects of Inorganic Chemistry" D. VanNostrand, N.Y. 1939 p 256

N.E.P.A. "Survey on Lithium Hydride" (?) (Not currently available to authors)

Bode "Zur Kenntnis des Lithiumhydrids" Z. physik.Chem.(B) 13, 99 (1931)

Peters - Z. anorg. Chem. 131,140,168 (1923)

1.03 Sources and Industrial Utilization

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

Metalloy Corp. Rand Tower, Michigan
Maywood Chemical Works, Maywood, N. J.

Possibly, The Foote Mineral Company of Pennsylvania also produces the metal but does not advertise it. 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 by reacting Li₂O with Mg under hydrogen.(8)The National Research Corp., Cambridge, Mass. has explored the possibility of large scale preparation of lithium metal, purification of lithium by vacuum distillation.(9)Additional data on lithium purification is available.(10)

The commercial lithium metal and the hydride prepared therefrom are sometimes contaminated with carbon, as graphite or as Li₂C₂ in solid solution; 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.

Both lump hydride and powder are available. Metalloy, Inc. supplies a -100 mesh 83% powder which assays over 95% LiH. Coarser powders are also available (through 3/8" screen) which may run over 98% LiH. Maywood Chemical Works supplies both lumps and powder of comparable purity.

Lithium hydride's major commercial use appears to be the manufacture of lithium aluminum hydride LiAlH_4 , which is widely used by the pharmaceutical industry. The manufacture of lithium aluminum hydride is wasteful of lithium as ordinarily practiced since three quarters of the lithium goes to lithium chloride in a form difficult to work commercially. Lithium hydride is also used in the manufacture of a few organic chemicals, etc. as a drying agent, as a metallurgical reagent, and for the manufacture of lithium amide. These uses are small for the most part.

Military and non-commercial uses appear to constitute the major utilization of lithium hydride. It is used by the Army as a portable lightweight source of hydrogen (by reaction with water) and for other purposes, e.g. pressurizing fuel tanks, etc. One process for the manufacture of diborane and related materials employs lithium hydride 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 Mathieson Chemical Corp.)

1.04 Preparation of Lithium Hydride.

The best available method is direct synthesis. Although lithium hydride may be formed in other ways none 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 used.

Clean a crucible or boat of 316 or 347 alloy stainless steel, bake dry and partially fill with lithium cut under a CO_2 atmosphere. Place the boat anaerobically in a stainless steel retort. Evacuate, heat to 100°C in vacuum. Admit hydrogen (purified by passage over uranium turnings) 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 CO_2 -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 (overnight 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.)

2.00 PHYSICAL PROPERTIES

2.01 Crystal Structure and X-Ray Scattering

The crystal structure of lithium hydride is face-centered cubic, of the sodium chloride type. The unit distance, established by the careful x-ray crystallographic studies of Zintl and Harder (12), Tronstad and Wergeland (13), and Ahmed (14) (15), is:

$$a_0 = 4.085 \pm 0.002 \text{ A.U.}$$

The earlier value of Bijvoet and Karssen (16) 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 (16) (17), 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 (12) (14) (18). The early work of Bijvoet and Karssen has been criticized by Zintl and Harder (12) (19).

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 (20). Lithium hydride has not yet been investigated in this way.

Lonsdale (21) 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 Q (Sect. 2.06). 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 (5) and Bode (22) 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 (23). 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

	d, g./ml.	V _m , ml./mol
Pycnometer, Moers	0.816 ± 0.004	9.74
Pycnometer, Bode	0.705 ± 0.02	11.27
He Densitometer, this lab.	0.788 ± 0.002	10.08
X-ray Crystallographic	0.7738 ± 0.0004	10.266

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 method, is:

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

Further research is needed to define the density more precisely.

2.03 Electrical Conductivity and Electrolysis

G. N. Lewis (4) 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 saltlike in nature. Preliminary experiments under his direction indicated that fused lithium hydride (m.p. 680°C., Ref.63) is a good conductor of electricity.

Moers (5) measured the electrical conductivity of lithium hydride at temperatures from 443°C. to 754°C., using both direct and alternating current, but obtaining consistent results only with the latter.

Table 2 below shows his results.

Table 2

Electrical Conductivity of Lithium Hydride

T°C.	443	507	556	597
Sp. Cond., ohms ⁻¹ cm ⁻¹	2.124×10^{-5}	2.154×10^{-4}	9.633×10^{-4}	3.665×10^{-3}
T°C.	657	685	725	754
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 °C. No discontinuity is noticeable at the melting point of 680°C.

Guntz and Benoit (24) 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 (25) 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° and 650°C., and when the hydrogen pressure was large enough to prevent dissociation of the lithium hydride.

Potter and Bockris () 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 (680°C.). At higher temperatures, or for longer times, the yield decreased.

2.04 Lattice Properties

2.041 Lattice Energy

The lattice energy has been calculated by Kasarnowsky (23) by means of the Born-Haber thermochemical cycle. The resulting value, as corrected by Sherman (28) is:

$$U = -218.0 \text{ kcal./mol}$$

Bradley (29) has also calculated the lattice energy both by means

of a theoretical calculation of the force constant of the lattice and by means of a cycle, obtaining the results $U = -230.5$ kcal./mol and $U = -245.2$ kcal./mol, respectively. The value of Kasarnowsky may be shown to more consistent with other theoretical calculations of the lattice energy (30).

2.042 Compressibility

The so-called Born repulsion coefficient of an ionic solid may be calculated from its lattice energy, and the coefficient of compressibility may be calculated from this repulsion coefficient. The value for lithium hydride is (27) (28):

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

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. The compressibility of lithium hydride has not been obtained experimentally.

2.043 Coefficient of Expansion

The coefficient of expansion of lithium hydride has not been determined experimentally, but has been calculated from lattice frequency considerations by Nordmann and Lipscomb (31). Their values are:

Linear coefficient of expansion: 3.9×10^{-5} per degree C.

Cubical " " " : 1.2×10^{-4} " " "

This is very close to the coefficient of expansion of NaCl of 1.21×10^{-4} .

2.044 Cohesive Energy

Lundquist and Froeman (32) have developed a method of calculating the cohesive energy of lithium hydride, but so far do not appear to have published their promised numerical results.

2.045 Lattice Frequency

Ubbelohde (33) has calculated the Debye characteristic temperature of lithium hydride, and thence the lattice frequency $\nu_{\max}$, from the low temperature heat capacity data of Guenther (34). The values are:

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

De Groot and Biedermann (35) 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.

2.046 Zero-Point Energy

Ubbelohde and de Groot and Biedermann (par. 2.045) have calculated

the zero-point energy of lithium hydride. Ubbelohde's value, based on Debye's continuum theory, is $E^0 = 1820$ cal./mol. DeGroot and Biedermann have 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 are $E^0 = 1120$ and 5490 cal./mol 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.

2.05 Nature of the Bonding in Solid Lithium Hydride

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 bonds in this solid.

Hylleras (30) 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./mol for the lattice energy (Kasarnowsky 218) and 4.42 A.U. for the lattice constant (experimental 4.085). Hylleras believes that a more elaborate wave function would improve the agreement on lattice distance without changing the lattice energy significantly.

Ewing and Seitz (36) have also calculated the electronic structure of solid lithium hydride by quantum mechanical methods. They report calculated electron density distributions about the hydrogen and lithium atoms in lithium hydride, and show that the effective charges on the ions are $Li^{+0.35} H^{-0.35}$.

Ahmed (14) (15) calculated effective charges on the ions in lithium hydride, based upon x-ray scattering data, corrected for thermal scattering by means of Lonsdale's (21) calculation of the root-mean-square amplitude of vibration. He found, assuming Li^+xH^-x , that $x = 0.25 \pm 0.25$.

All of these indicated that the lithium-hydrogen bond in solid lithium hydride is considerably covalent, and may actually be more covalent than ionic. Also, if the ionic radius of Li^+ is taken as the normal value of 0.60 A.U. of Pauling (37), then the radius of the hydride ion is 1.44 A.U. This is smaller than the hydride ion radius of 1.51 ± 0.03 A.U., obtained for the other alkali metal hydrides (12) again based on Pauling's ionic radii. This shorter distance indicates tighter bonding, giving additional support to the partial covalency of the bond. Additional information about the lithium-hydrogen bond has been obtained from studies of the properties of the gaseous LiH molecule. This is discussed in Section 2.08.

2.06 Thermodynamic Properties

2.061 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(63) by Moers (5), and by Messer and Fasolino (38) in this laboratory. The results are given and compared in Table 3 below.

Table 3

Heat of Hydrolysis and Heat of Formation of Lithium Hydride

ΔH , kcal./mol at 25°C., infinite dilution.

	Heat of Hydrolysis	Heat of Formation
Guntz	- 31.6	- 21.6
Moers	- 31.1	- 21.6
Messer and Fasolino	- 31.76 $\pm$ 0.06	- 21.34 $\pm$ 0.12

The measurements of Guntz and Moers were made in open Dewar flask calorimeters, the hydrogen gas being allowed to escape. Those of Messer and Fasolino were carried out in a closed bomb calorimeter (the hydrogen thus being confined), and the measurements of temperature rise were made with a calibrated platinum resistance thermometer.

2.062 Heat Capacity

The heat capacity of lithium hydride has been measured by Guenther (34) over the comparatively narrow low temperature range from 74°K. to 90°K., and also at room temperature, 293°K. As shown by Ubbelohde (33), these data fit fairly well a Debye heat capacity curve, with the characteristic temperature $\Theta = 815 \pm 10$. The 20°C. values are:

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

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

Because of the high Debye Θ , and hence high lattice frequency, lithium hydride should not achieve its full classical (Dulong and Petit) heat capacity of 12-13 cal/mol-deg. until the temperature is somewhat above 815°K., or 542°C. Hence the specific heat of lithium hydride should increase by 50% or more between room

temperature and the melting point of 680°C., most of the increase coming during the first portion of this range.

2.063 Entropy; Free Energy of Formation

Kelley (39) has calculated the entropy of lithium hydride at 298°K., from Guenther's heat capacity data. The free energy of formation may then be calculated, using this figure and the heat of formation of Messer and Fasolino, Table 3. The resulting values are:

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

$$\Delta F^\circ = -16,450 \pm 300 \text{ cal./mol at } 298^\circ\text{K.}$$

2.064 Melting Point, Heat of Fusion

The melting point of lithium hydride, as determined by Guntz (63) is 680°C. This value has been confirmed several times by later workers. No measurements of latent heat of fusion have been made, and no basis for its estimation is to be found in the literature. The fact that no discontinuities are to be noted in the curves of hydrogen dissociation pressure vs. temperature (Sect. 3.02) at the melting point indicates that the latent heat of fusion is probably small. McKisson (40) reports that the shrinkage of volume of lithium hydride on solidifying from the melt is estimated to be 16%.

2.07 Optical Properties

2.071 Refractive Index

The refractive index of crystalline lithium hydride was measured by Bode (22) by the method of immersion in liquids of known refractive index. The value found was:

$$n_D = 1.615 \pm 0.002^* \text{ (room temp.)}$$

2.072 Absorption Spectrum

The absorption spectrum of crystalline lithium hydride in the ultra-violet was observed by Kapustinsky, Shamovsky, and Bayushkina (41) (42) and by Bach and Bonhoeffer (43) (44). Both groups of workers found a sharp absorption maximum at $2517 \pm 2 \text{ A.U.}$ In addition, Bach and Bonhoeffer observed a diffuse absorption band, beginning at 1900 A.U. and extending to shorter wave lengths.

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 2.08.

2.073 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-

*Stavitzky, Walker and Ellinger (90) have measured the refractive indices at several wave lengths of lithium hydride and lithium deuteride by the refraction of prisms cut from the crystalline materials. They find a quite different set of values: $n_D = 1.9847 \pm 0.0005$ for LiH, and $n_D = 1.9856 \pm 0.0006$ for LiD.

blue (5) (45) (43) (44). Ultraviolet light produces the blue color more rapidly. No measurable hydrogen loss by decomposition is noticeable, although it is reported (5) 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. (44). Albert and Mahe (46) 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 (43) (44) 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 (43) (44) (41) (42):

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 (44).

2.08 Lithium Hydride Gas

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 molecules of lithium hydride gas, LiH. Some emission lines may also be found. Many properties of the LiH molecule and of the lithium-hydrogen bond have been deduced from interpretation of the spectroscopic studies and from fundamental quantum mechanical calculations on this relatively simple diatomic molecule.

The absorption and emission spectra of gaseous LiH have been observed by Nakamura (47) and by Crawford and Jorgensen (48). Over 1000 lines, in 26 bands, have been observed, covering the range from 3100 to 4500 A.U. Most of these lines have been assigned to definite quantum transitions between energy levels in the upper and lower electronic states of the molecule.

Certain properties of the LiH molecule have been deduced from analysis of the band spectrum, along with other considerations. These are tabulated below, with references.

Equilibrium internuclear distance: $r_0 = 1.60$ A.U. (47)(49)

Dissociation energy (normal atoms): $H_D = 59$ kcal./mol (47)(49)(50)

Moment of inertia (ground state): $I = 3.70 \times 10^{-40}$ gm. cm.² (47)

Fundamental vibration frequency: $\nu = 1405.65$ cm.⁻¹ (49)

Dipole moment: $\mu = 4.05$ Debyes (49); 3.5 D (51).

2.084 Thermodynamic Properties

Certain thermodynamic properties of the LiH molecule at 298°K. have been calculated in the "Selected Properties" of the National Bureau of Standards (52). These are:

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

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

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

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 where solid LiH is stable at 1 atm. pressure. This concentration should be susceptible to calculation by statistical mechanical methods from band spectrum data.

The lithium hydride gas molecule has been the subject of considerable theoretical study by quantum mechanical methods. Among others, the papers of Fischer (53) (54), Mueller and Eyring (55), Mulliken (56), and Knipp (57) may be cited. None of these seem to give excellent agreement with experimental values in both dissociation energy and bond distance values. The calculations of Mueller and Eyring (55) are of interest in that they give a picture localizing 11% of the electronic charge of the two binding electrons on the Li atom, 66% on the H atom, and 23% in the overlap. This would correspond roughly to $\text{Li}^{+0.55}\text{H}^{-0.55}$. For an internuclear distance of 1.6 A.U., this would give a dipole moment of 4.2 D, close to the values in 2.083.

2.09 Lithium Deuteride

While lithium deuteride has not been investigated as thoroughly as lithium hydride, some information on its properties has been accumulated. Table 4 below gives the comparative properties of the two compounds. In almost all cases, the workers measuring or calculating the value tabulated for LiD used the same method as they did for LiH (see earlier sections of this report).

Table 4

Comparative Properties of Lithium Hydride and Lithium Deuteride

	LiH	LiD	Reference
Lattice constant, A.U.	4.085	4.065	(58)(13)
Density, g./cm. ³ (x-ray)	0.7738	0.8849	" "
Molar volume, cm. ³ /mol (x-ray)	10.27	10.13	
Melting point, °C.	680	686	(13)
Root-mean-square amplitude of vibration, A.U.	0.24	0.29	(21)
Debye Θ	815	611	(33)
Zero-point Energy, kcal./mol			
Ubbelohde, Debye theory	1.82	1.37	(33)
de Groot and Biedermann, London method	1.12	0.59	(35)
de Groot and Biedermann, Born method	5.49	4.30	(35)
Cubical Coefficient of Expansion, °C. ⁻¹ x 10 ⁻⁴	1.2	1.7	(31)
Band Spectrum, gas	Ref. (48)	Ref. (59)	

Tronstad and Wergeland (60)(61) have carried out a series of thermodynamic estimations on lithium hydride and lithium deuteride, using Ubbelohde's (33) zero-point energy and Debye Θ values, along with known information on lithium metal, H₂ gas, and HD gas, to estimate the free energy of formation and the dissociation pressure (see sect. 3.01) of lithium hydride and lithium deuteride at temperatures up to 900°K. From these, they have calculated the equilibrium constants of the following exchange reaction at a series of temperatures.

T°K.	298.1	400	500	600	700
K _p	1.34	1.65	1.7	1.8	1.9

3.00 FORMATION, DISSOCIATION, AND PHASE EQUILIBRIA

3.01 Rate of Formation and Decomposition

Quantitative data on the rate of reaction of lithium with hydrogen are relatively scarce. Albert and Mahe (46) 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 (62) 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 5 below, but these do not fit an easily describable general pattern.

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. At a higher temperature, the reaction proceeds rapidly to virtual completion. Table 5 below summarizes the observations of the various workers.

Table 5
Rate of Formation of Lithium Hydride

	Temp. of first reaction	Temp. of rapid reaction
Guntz (3)	Just before red heat	Full red heat
Dafert and Miklausz (45)	440°	700°
Ephraim and Michel (64)	300°	580-660°
Soliman (65)	500°	----
Bode (22)	450-500°	700°
Albert and Mahe (46)	450°	680-690°

The interpretation of this behavior is clear in terms of the dissociation pressure behavior to be described in section 3.02 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 680°.

There is some evidence that lithium metal will take up hydrogen at a lower temperature under certain circumstances. Remy-Gennete (66) 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 (67) 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 (67) 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°. 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.

*In view of the fact that the vapor pressure of lithium metal is only about 10^{-10} mm. at 190°C. (Ref. 71), we are inclined to doubt the possibility of sublimation.

3.02 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 follows the van't Hoff isochore, as represented by the approximately linear plots of logarithm of pressure vs. reciprocal of absolute temperature shown in Figure 2. The variation of dissociation pressure with composition at constant temperature is shown in Figure 1.

The explanation of the shapes of the isotherms in Fig. 1 is as follows: The dissociation pressure of the hypothetical completely pure stoichiometric lithium hydride is very high. The removal of small amounts of hydrogen produces a large decrease in pressure, the liberated lithium metal going into solution in the hydride, which remains a single phase. When enough hydrogen has been withdrawn to saturate the lithium hydride with lithium metal, the pressure becomes independent of further change of composition, a second phase, lithium rich, separating out. The constant pressure in this two-phase region of varying composition is the so-called "plateau" pressure. When enough 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 lithium metal 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 (64), Tronstad and Wergeland (13) and Peters (25) 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 by Johnson and Hill (68), Johnson and Perlow (62), and Gibb (7). The isotherms of Johnson and Hill at 700°, of Johnson and Perlow at 800°, and of Gibb at 800°, 900°, and 1000° are shown in Figure 1. The corresponding numerical data appear in Table 6. 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%. All percentages have been corrected to 100% purity by assuming the impurities to be inert.

Table 6

Dissociation Pressures of the Lithium-Hydrogen System

Johnson and Hill, 700°C.

Wt. % LiH	2.7	2.7	5.4	8.4	11.5	14.2	16.3	20.2	26.5
PH ₂ , 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				
PH ₂ , mm.	35.0	35.0	35.0	35.0	268.0				

Johnson and Perlow, 770°C.

Wt. % LiH	2.2	3.5	5.0	7.4	10.6	17.5	23.7	25.6	35.6
PH ₂ , 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
PH ₂ , 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			
PH ₂ , mm.	164.0	154.5	161.0	193.0	211.5	317.5			

Johnson and Perlow, 825°C.

Wt. % LiH	5.2	7.5	11.3	17.2	28.0	40.3	54.4	64.2	72.7
PH ₂ , 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			
PH ₂ , mm.	442.0	424.0	442.0	487.0	549.0	714.0			

Gibb, PH₂, mm.

% 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

The results of Gibb are seen to be higher than those of Johnson and Perlow for 100% and for 98.9% lithium hydride, and lower for 96.4% hydride and less.

The plateau regions, from the curves of Johnson and Hill and Johnson and Perlow, are seen to become distinctly shorter with increasing temperature, indicating increasing mutual solubility of hydride and metal.

The dissymmetry of the plateaus would indicate that hydrogen is more soluble in lithium metal, than is lithium metal in lithium hydride.

It is to be noted from Figure 1 that, for low percentages of lithium hydride, the dissociation pressures seem to approach the same values at all three temperatures, within experimental error. Hence the pressure values to the left of the plateaus are probably unreliable.

The estimated plateau regions and pressures are:

- 700°C. (Johnson and Hill) : 18-96% LiH , p = 35.0 mm.
 770°C. (Johnson and Perlow) : 36.91% LiH , p = 153 ± 6 mm.
 825°C. (Johnson and Perlow) : 60-93% LiH , p = 436 ± 8 mm.

The shortness of the 825° plateau, and the rapidly increasing rate of shortening with temperature, indicate the possibility of a critical point at a temperature not too much higher. Above this temperature hydride and metal would be totally miscible to form only one homogeneous phase. Such a critical point is known for the palladium-hydrogen system (59) and others.

The curves of Gibb, on the other hand, indicate shorter plateaus (greater solubility of lithium in lithium hydride), lower plateau pressures, and a higher critical temperature, as compared with the results of Johnson and coworkers. The following tabulation assumes that at 900°C. Gibb's 86.4% and 91.4% points are probably both on the plateau, while at 1000°C. only the 86.4% point is on the plateau.

- 900°C. p = 490 ± 70 mm.; plateau ends at 94 ± 2% LiH
 1000°C. p = 2000 mm.; plateau ends at 88 ± 3% LiH

The plateau pressures have been measured by Hurd and Moore (70) as well as by the workers already discussed. Johnson and Hill also made some plateau measurements below 700°C., as well as at 700°. The following empirical equations represent the results of these various researches on the plateau pressures, and Table 7 lists the pressure values calculated from these equations at 600°, 700°, and 800°. The values in parentheses are beyond the temperature limits of the data on which the equations are based.

Hurd and Moore, 509-655°C.	$\log P_{\text{mm.}} = -9600/T^{\circ}\text{K.} + 11.227$
Johnson and Hill, 578-728°C.	$\log P_{\text{mm.}} = -10320/T + 12.165$
Johnson and Hill;	
Johnson and Perlow, 700-825°C.	$\log P_{\text{mm.}} = -9337/T + 11.131$
Gibb, 900-1000°C.	$\log P_{\text{mm.}} = -8800/T + 10.20$

Table 7

Plateau Pressures of Lithium-Hydrogen System

	Hurd and Moore	Johnson, Hill and Perlow	Johnson and Hill	Gibb
600°C.	1.7 mm.	(2.7 mm.)	2.2 mm.	(1.3 mm.)
700°C.	(22.9 mm.)	34.2 mm.	36.2 mm.	(14 mm.)
800°C.	(190 mm.)	268 mm.	(352 mm.)	(100 mm.)
t°C. at which p = 760 mm.	879°	859°	841°	929°

The plots of logarithm of pressure vs. reciprocal of absolute temperature for the plateaus and for certain other compositions, are shown in Figure 2. The pressures plotted are interpolated for the particular composition values from the smooth curves of Figure 1.

3.03 Other Phase Equilibria

3.031 Lithium-Lithium Hydride Solid-Liquid Equilibrium

The equilibrium diagram for this system, which would enable the prediction of the melting and freezing behavior of mixtures of lithium and lithium hydride, has not been determined experimentally. Its determination by the method of time-temperature cooling curves is being undertaken in this laboratory. Because of its importance, a discussion of a probable hypothetical diagram (Figure 3) is included here.

The ends of the plateaus of Johnson and Hill (68) and Johnson and Perlow (62) enable the prediction of the compositions of the two mutually saturated liquid phases at and above 700°C . The lithium-rich phase, probably a solution of hydrogen in lithium, is denoted as the alpha phase, and the lithium hydride-rich phase, probably a solution of lithium metal in lithium hydride, is denoted as the beta phase. The designations s and l stand for solid and liquid, respectively.

Pure lithium hydride has a freezing point of 680°C . The addition of lithium metal probably lowers the freezing point of the hydride, the solid phase β (s) separating out being a solid solution of Li in LiH, of lower % Li than the liquid phase with which it is in equilibrium.

At the temperature T_{β} , the saturated β (l) phase reaches its equilibrium freezing point, and only solid β -phase can exist below this temperature. All mixtures in the plateau region of composition should show an arrest in their cooling curves at this temperature. T_{β} should not be too far below 680° , since Li metal is soluble in LiH only to an extent of less than 2%, according to Johnson and Hill's diagram. However, if the latent heat of fusion is very low, as mentioned in Sect. 2.064, the freezing point depression constant of lithium hydride would be high. In such a case, T_{β} should be significantly below 680°C .

For a long temperature range from T_{β} to T_{α} , all plateau compositions should consist of a solid β -phase and a liquid α -phase, of gradually decreasing mutual solubility with decreasing temperature. At the temperature T_{α} , the saturated α -phase reaches its freezing point, and below T_{α} only solid α (s) and β (s) phases exist.

The temperature T_{α} is probably a eutectic, below the freezing point of pure Li metal of 180.5°C . (71) For metal-hydrogen systems where a metallic hydride is formed, the square root of the dissociation pressure is typically proportional to the concentration of hydrogen in the metal for small additions of hydrogen to metal, indicating that the hydrogen goes into solution as atomic hydrogen (or protons) (72). If this were also true for the saline type of hydride

system, with which we are dealing here, the freezing point of lithium would almost surely be lowered by the addition of hydrogen. Only if the hydrogen in the lithium were largely combined to form LiH would the freezing point of lithium be raised by hydrogen.

3.032 Lithium Hydride-Lithium Fluoride System

Of all systems of lithium hydride with other similar ionic compounds, only the system lithium hydride-lithium fluoride has been studied, and this system only in a fragmentary way.

Zintl and Harder (12) investigated the x-ray diffraction pattern of a mixture of LiH and LiF of 73 mol % LiH, solidified from the melt. Both sets of lines were observed, indicating incomplete miscibility. The unit distance a^0 for LiH was not appreciably modified (4.084 A.U. for pure LiH; 4.087 ± 0.003 in mixture). However, the a^0 value for LiF was modified (4.019 A.U. pure; 4.039 ± 0.003 in mixture). Thus the solids do not mix completely, even though their structures are identical and their lattice constants differ by only 1.5%. The modification data might be interpreted as indicating that LiH is more soluble in LiF, than is LiF in LiH.

Gibb (7) measured the dissociation pressure of a mixture of lithium fluoride and lithium hydride, of 85.4 mol % LiH. The results below show that at all temperatures the dissociation pressures of the mixture are lower than those of "100%" LiH by the same author, and at 800°C. and 900°C. they are even lower than the probable plateau values. This would be expected if there were some solubility of the fluoride in the hydride.

Dissociation Pressure of Mixture of LiF and LiH of 85.4 Mol % LiH

T°C.	Pmm.
800	85
900	345
1000	2477

4.00 Chemical Properties

(See also general treatment in paragraph 1.01) The chemical behavior of lithium hydride is only qualitatively similar to that of 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 reductions, but more vigorous in organic reductions where its covalent nature is important. Hurd (73) reports a vestigial solubility in ethers which, if true, helps 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°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: $MO + 2Li \rightarrow Li_2O + M$ is greater than that of: $MO + 2LiH \rightarrow Li_2O + M + H_2$ by the heat of the reaction $2LiH \rightarrow 2Li + H_2$. As noted above the latter heat is quite significant being endothermic by 44 Kcal at room temperature and by half this order of magnitude (roughly) 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 metallurgical reducing agent than calcium. This is also true of the hydrides despite the higher heat of formation of calcium hydride. The volatility of lithium oxide, however, favors reductions by permitting removal of this product from the equilibrium: $MO + 2Li \rightarrow M + Li_2O$.

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 (220 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 shown by e.g. aluminum hydride and lithium aluminum hydride in their organic reactions.

4.01 Reaction of lithium hydride with water and air.

The finely powdered hydride reacts rapidly with air of low humidity forming Li_2O , $LiOH$ and Li_2CO_3 as noted above. 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 1" 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 usually 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 Chemical Corps, Signal Corps, and Navy reports issued during the war and not currently available to the authors. The rate studies are very complicated owing 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. (74) The heat of the reaction $\text{Li} + \text{H}_2\text{O} \rightarrow \text{LiOH} + \text{H}_2$ is 31.4 Kcal for liquid water and 31.1 Kcal for water vapor. (Our value for liquid water is 31.8)

4.02 Reactions with acidic substances.

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

In the absence of moisture, the hydride reacts with surprising reluctance with HCl and Cl₂, a temperature of 500°C being required to complete the reaction. Sulfur dioxide reacts readily yielding the thiosulfate and, above 50°C, the sulfide. (75) Boron trichloride and silicon tetrachloride in ether solution react with lithium hydride yielding lithium chloride and diborane or silane respectively. Titanium tetrachloride does not appear to react. Boron trifluoride reacts with heated lithium hydride to give diborane. Silicon dioxide reacts readily at red heat giving a brown glassy material presumably containing silicon or 'silicon monoxide' and 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.

4.03 Reactions with basic substances.

Ammonia reacts very slowly with lithium hydride at room temperature or below but rapidly above 300°C yielding the amide LiNH_2 quantitatively. It's presumed analagous reaction with primary and secondary amines has 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 abovementioned reaction should go to completion at temperatures where MH is largely dissociated. Continued removal of hydrogen should force this reaction to virtual completion, viz. $2\text{LiH} + \text{M}_2\text{O} \rightarrow \text{Li}_2\text{O} + 2\text{MH} \rightarrow 2\text{M} + \text{H}_2$. Lithium oxide may coexist with lithium hydride, no formation of water being accomplished. Lithium hydroxide reacts irreversibly with lithium hydride presumably forming the oxide and hydrogen:

It seems likely that other hydroxides act similarly (although sodium hydroxide fails to react with sodium hydride and rather forms a solution. (76) There is also a possibility of methathesis followed by reaction of lithium hydride with the lithium hydroxide formed.

4.04 Reaction of Lithium Hydride with Organic Compounds

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 does effect reduction of acid chlorides to aldehydes and accomplishes partial reduction of several easily reducible substances. (77) 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.

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. (78) (79)

Presumably no reaction occurs with silicone rubbers, but this has not been established experimentally.

4.05 Miscellaneous Reactions of Lithium Hydride

The older literature cites a reaction with lithium chloride at red heat yielding a "subchloride". (80) Sodium chloride is reduced, in part, at red heat owing to the removal of the volatile components, sodium metal and lithium chloride. Molten systems containing Na, Li, H, LiCl and NaCl are presumably formed first. The oxides and halides of many metals are reduced at red heat or above, some violently. Thus, palladium chloride reacts almost explosively.

Magnesium chloride is probably first reduced to magnesium hydride which then decomposes. Metals which form hydrides which are stable at red heat (Ti, Zr, Ta) may yield hydrides via these reactions. The reduction of silicon dioxide is mentioned earlier.

The reduction of carbon dioxide has not been investigated as thoroughly as in the case of sodium hydride, but it seems likely that, at high temperatures, lithium formate and, ultimately, lithium carbide may be formed. Carbon reacts with lithium hydride but the reaction has not been studied. Presumably lithium carbide is formed together with hydrogen or methane, etc. 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.

The reaction with group III halides has been mentioned earlier. This results in the formation of a double hydride, e.g. $LiBH_4$, $LiAlH_4$, or the reaction is in effect metathetical leading to LiCl and, e.g. $(BH_3)_2$, $(AlH_3)_n$, etc. (81)

Triphenylboron reacts by addition. On fusing LiH with $(C_6H_5)_3B$, $(C_6H_5)_3BHLi$ is formed. (82) It is probable that many reactions of LiH involve a preliminary addition of this type as a first step.

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. (Bi, Sb, Sn, Pb, Tl). 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 $800^\circ C$.

Electrolysis of solid lithium hydride yields hydrogen at the anode and lithium at the cathode. (26) Lithium hydride in molten LiCl-KCl eutectic behaves similarly. (83) Lithium hydride exchanges readily with deuterium and tritium. (84).

4.06 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. (7)

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 (85)

The tendency of lithium to alloy with various metals is discussed in the "Liquid Metals Handbook" and in the older literature. (86)

4.07 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.

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.S.I. 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.

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%. (40) 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.

4.08 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 (87) 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 (88) 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 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.

4.09 General Procedures for the 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. 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.

Nitrogen is determined by Kjeldahl distillation, the solid hydride being placed in the distillation flask to which ice water is added anaerobically. 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 and boric acid method is recommended.

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

Carbonate carbon has not been determined by the authors but presumably may be handled by classical means, e.g. sweeping the acidified hydrolysate with inert gas which then passes through aqueous barium hydroxide. Lithium carbonate and sulfate are very sparingly soluble and the evolution mixture would have to be acidified (with hydrochloric acid) and boiled to ensure complete evolution of CO_2 . We have determined total carbon by combustion, but do not recommend this method. The entire silica combustion tube must be protected from lithium oxide vapor or 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. Owen's (89) spectrographic technique 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, calcium, magnesium, boron, etc.

Lithium oxide has not been determined by the authors. Presumably the same method could be used as for oxide in lithium, viz. (85) dissolving in absolute ethyl alcohol and filtering off the insoluble oxide. (The latter is usually accompanied by some nitride which is determined by Kjeldahl and subtracted.) The oxide is determined by titration with standard acid.

Determination of total lithium does not appear useful in view of the ease and precision of the determination of total hydrogen by evolution. Difference between total hydride by evolution and total base by titration of the hydrolysis residue permits a rough calculation to be made of lithium metal and lithium hydride contents, but this is subject to obvious errors unless a correction is made for other bases which may be present. If it is assumed that the only other base is Li_2O a useful approximation of the LiH , Li and " Li_2O " contents may be calculated by solution of three simultaneous equations, viz:

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

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

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

REFERENCES

-30-

- (1) Report ANL-4208, Oct. 4, 1948.
- (2) Hautefeuille, P. and Troost, L., Ann. Chim. Phys. (5) 2, 273 (1874).
- (3) Guntz, A., Compt. rend. 122, 244-6 (1896)
- (4) Lewis, G. N., J. Am. Chem. Soc. 38, 762-85 (1916).
- (5) Moers, K., Z. anorg. allgem. Chem. 113, 179-228 (1920).
- (6) Dafert, F.W. and Miklausz, R., Monatsh. 30, 649 (1909).
- (7) Gibb, T.R.P., unpublished, 1950. See Report NEPA 1841, April 30, 1951.
- (8) Alexander, P.P., U.S. Patent 2,606,100, Aug. 5, 1952. See also 2,408,748, Oct. 8, 1946.
- (9) Stauffer, R.A., "Report of Lithium Research", O.S.R.D., January, 1944 et seq.; cf. also Patent U.S. 2,424,512, July 22, 1947.
- (10) Rogers, R.R. and Viens, G.E., Trans. Can. Inst. Mining Met. 438, 623-8 (1948). See also review on Li production, ibid, p. 619.
- (11) Baker, P.S., Duncan, F.R., and Green, H.B., Science 118, 778 (1953) (Reference to purification by vacuum treatment)
- (12) Zintl, E. and Harder, A., Z. physik. Chem. B14, 265-84 (1931).
- (13) Tronstad, H. and Wergeland, H., Kgl. Norske Videnskab Selskab Forh. 10, No. 10, 36-39 (1937).
- (14) Ahmed, M.S., Nature 165, 246 (1950).
- (15) Ahmed, M.S., Phil. Mag. 42, 997-1004 (1952).
- (16) Bijvoet, J.M. and Karssen, A., Proc. Acad. Sci. Amsterdam 25, 27-30 (1922).
- (17) Bijvoet, J.M., Rec. trav. chim. 42, 859-903 (1923)
- (18) Bijvoet, J.M. and Frederikse, W.A., Rec. trav. chim. 48, 1041-6 (1929).
- (19) Zintl, E. and Harder, A., Z. physik. Chem. B15, 416 (1932).
- (20) Davidson, W.L., Morton, G.A., Shull, G.G., and Wollan, E.O., Report MDCC-842, declassified April 28, 1947.
- (21) Lonsdale, K., Acta Cryst. 1, 142-9 (1948).
- (22) Bode, H., Z. physik. Chem. B13, 99-104 (1931).
- (23) Schumb, W.C. and Rittner, E.S., J. Am. Chem. Soc. 65, 1692-5 (1943).
- (24) Guntz, A. and Benoit, F., Compt. rend. 176, 970-1 (1923).

- (25) Peters, K., Z. anorg. allgem. Chem. 131, 140-72 (1923).
- (26) Potter, E.C. and Bockris, J. O'M., Colloques intern. centre natl. recherche sci. (Paris) 39, Electrolyse C3-C6 (1952); Chem. Abstr. 47, 5280 (1953).
- (27) Kasarnowsky, J., Z. Physik 61, 236-8 (1930).
- (28) Sherman, J., Chem. Reviews 11, 93-170 (1932).
- (29) Bradley, R.S., Phil. Mag. 7, 1081-4 (1929).
- (30) Hylleras, E.A., Z. Physik 63, 771-94 (1930).
- (31) Nordmann, C.E. and Lipscomb, W.N., J. Chem. Phys. 21, 2077 (1953).
- (32) Lundqvist, S.O. and Froeman, P.O., Arkiv. Fysik 2, 431-8 (1950).
- (33) Ubbelohde, A.R., Trans. Faraday Soc. 32, 525-9 (1936).
- (34) Guenther, P., Ann. Physik 63, 476 (1920).
- (35) De Groot, S.R. and Biedermann, M.M., Physica 8, 905-22 (1941).
- (36) Ewing, D.H. and Seitz, F., Phys. Rev. 50, 760-77 (1936).
- (37) Pauling, L., "Nature of the Chemical Bond", p. 326, Cornell University Press, Ithaca, New York, 1939.
- (38) Messer, C.E., and Fasolino, L.G., Report NYO-3956, March 15, 1954.
- (39) Kelley, K.K., U.S. Bureau of Mines Bulletin 434, (1941).
- (40) McKisson, R.L., Report UCRL-992, Nov. 8, 1950.
- (41) Kapustinsky, A.F., Shamovsky, I.M., and Bayushkina, K.S., Acta Physico-chimica U.S.S.R. 7, 799-810 (1937).
- (42) Kapustinsky, A.F., Shamovsky, L.M., and Bayushkina, K.S., J. Phys. Chem. U.S.S.R. 10, 620-6 (1937).
- (43) Bach, F., and Bonhoeffer, K.F., Naturwissenschaften 20, 940 (1932).
- (44) Bonhoeffer, K.F. and Bach, F., Z. physik. Chem. B23, 256-64 (1933).
- (45) Dafert, F.W. and Miklauz, R., Monatsh. 33, 63-9 (1912).
- (46) Albert, P. and Mahé, J., Bull. soc. chim. France 1950, 1165-7.
- (47) Nakamura, G., Z. Physik 59, 218-42 (1929).
- (48) Crawford, F.H. and Jorgenson, T., Phys. Rev. 47, 932-41 (1935).

- (49) Klemperer, W.A. and Margrave, J.L., J. Chem. Physics 20, 527 (1952).
- (50) Gaydon, A.G., "Dissociation Energies and Spectra of Diatomic Molecules", Dover Publications, Inc., New York, 1950.
- (51) Adamov, M.N., Zhur. Fiz. Khim. 23, 1172-6 (1949); Chem. Abstr. 44, 1296 (1950).
- (52) Rossini, F.D. et al: "Selected Values of Chemical Thermodynamic Properties". National Bureau of Standards Circular 500, U.S. Govt. Printing Office, Washington, D.C., 1952.
- (53) Fischer, I., Nature 168, 1002 (1951)
- (54) Fischer, I., Arkiv. Fysik 5, 349-76 (1952).
- (55) Mueller, C.R. and Eyring, H., J. Chem. Phys. 19, 934-8 (1951).
- (56) Mulliken, R.S., Phys. Rev. 50, 1028-40 (1936).
- (57) Knipp, J.K., J. Chem. Physics 4, 300-07 (1936).
- (58) Zintl, E. and Harder, A., Z. physik. Chem. B28, 478-80 (1935).
- (59) Crawford, F.H. and Jorgensen, T., Phys. Rev. 47, 358-66 (1935).
- (60) Wergeland, H., Kgl. Norske Videnskab Selskab Forh. 10, 56-9 (1937).
- (61) Wergeland, H., ^{Kgl.} Norske Videnskab Selskab Forh. 10, No. 16, 60-63 (1937).
- (62) Johnson, W.H.; Thesis of Perlow, M.R.J., University of Chicago, 1941.
- (63) Guntz, M., Compt. Rend. 123, 694-6 (1896).
- (64) Ephraim, F. and Michel, E., Helv. Chim. Acta 4, 900-24 (1921).
- (65) Soliman, A., J. Applied Chem. (London) 1, 98-104 (1951).
- (66) Remy-Genneté, P.A., Ann. Chim. 19, 263-424 (1933).
- (67) Huettig, G.F. and Krajewski, A., Z. anorg. allgem. Chem. 141, 133-60 (1924).
- (68) Johnson, W.C.; Thesis of L.L. Hill, University of Chicago, 1938.
- (69) Gillespie, L.J. and Galstaun, L.S., J. Am. Chem. Soc. 58, 2565-73 (1936).
- (70) Hurd, C.B. and Moore, G.A., J. Am. Chem. Soc. 57, 332 (1935).
- (71) Douglas, T.B., Epstein, L.F., Dever, J.L., and Howland, W.H., National Bureau of Standards Report 2879, Oct. 16, 1953.
- (72) Sieverts, A., Z. physik, Chem. 88, 103 (1914).

- (73) Hurd, D.T. "Chemistry of the Hydrides". John Wiley and Sons, New York, 1952, p. 27.
- (74) Flood, H., cf. Chem. Abstr. 29, 4998 (1935).
- (75) Gmelin "Handbuch der anorganische Chemie", 8th ed. et seq. Verlag Chemie, Berlin, 1927; Hurd, loc. cit., p. 28.
- (76) Hansley, V.L., Chem. Eng. News 23, 1332 (1945).
- (77) Brandt, P., Acta Chim. Scand. 3, 1050-7 (1949).
- (78) Miller, A.J., Report TID 3032, Feb. 10, 1948.
- (79) Davidson, W.L., B. F. Goodrich Co., Contract AT(40-1)1309, 1951 et seq.
- (80) Gmelin, loc cit.
- (81) Schlesinger, H.I. et al, J. Am. Chem. Soc. 73, 4585 (1951) et seq.
- (82) Wittig, G. and Ruckert, A., Ann. 566, 101 (1950).
- (83) Bardwell, D.C., J. Am. Chem. Soc. 44, 2499 (1922).
- (84) Kaplan, L. and Wilzbach, K.E., Report AECD-2953.
- (85) "Liquid Metals Handbook", R.D. Lyon, Ed., Second Edition, 1952, p. 106. Supt. of Documents, Washington, D.C.
- (86) Masing and Tammann, Z. anorg. allgem. Chem. 67, 187 (1910).
- (87) Gibb, T.R.P., NEPA Topical Report No. 5, Oct. 12, 1950.
- (88) NEPA 1841 (Ref. 7), p. 26.
- (89) Owen, L.E. and Ellenburg, J.Y., Anal. Chem. 23, 1823 (1951).
- (90) Stavitsky, E., Walker, D.I., and Ellinger, F.H., Report LA-1559, Aug. 5, 1953.

Fig. 1--Dissociation pressures of lithium-lithium hydride system.

Fig. 2--Log P,MM. vs. $1/T^{\circ}K$. lithium-lithium hydride system.

Fig. 3--Solid-liquid equilibrium diagram lithium-lithium hydride system hypothetical.