LOS ALAMOS SCIENTIFIC LABORATORY

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THE PREPARATION OF PURE LITHIUM HYDRIDE

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1. Introduction

Between November 1948 and June 1950, Group CMR-2 had the task of investigating the chemical and physical properties of low molecular weight compounds containing hydrogen.* Lithium hydride was one of the compounds investigated which proved to be of interest. Early in 1951, CMR-2 undertook to develop a good method for preparing LiH (or LiD or LiT) in quantities ranging from about 100 g. to about 1 kg. This report contains the results of the investigations, and covers the period from August 1951 to April 1952.

The standard textbook method for LiH synthesis is direct combination of the elements at 500 to 600°C. and moderate pressures of hydrogen.** It has also been reported that LiH may be formed by the action of atomic hydrogen on lithium films.*** Patented processes**** generally are modifications of the direct union method.

By suspending the metallic lithium in a finely divided state in some liquid such as paraffin, oil, or fatty acid, LiH can be obtained at a much lower temperature, providing a high pressure of hydrogen is used. The reaction will then proceed at 250 to 400° instead of 500 to 600°C. A unique method***** consists of reducing anhydrous LiOH with some metal such as magnesium or aluminum at 300°C.

None of the commercial processes seems practical for LiT because of the high pressures involved or the exchange between the tritide or tritium gas and the liquid hydrocarbon. The preparation by reduction of LiOH is out of the question unless some method of separating LiH from the solid reaction mixture can be devised. Lithium hydride is not soluble in inert solvents.

Of the laboratory methods, only the direct union of the elements appears feasible. Consequently, only direct synthesis has been studied in this investigation.

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* Challenger et al., Los Alamos Scientific Laboratory Report LA-1215, June 1950.

** Albert and Mahĕ, Bull soc. chim. France, 1950, 1165-1167.
Zinlt and Garder, Z. phyzik Chem., B14, 265 (1931)

*** Ferrell, Pearson and Robinson, J. Chem. Soc. 1934, 7-8.

**** U. S. Patents Nos. 2,401,323, 2,401,326, and 1,958,012.
British Patents Nos. 276,313 and 283,089.

*****U. S. Patent No. 2,450,266.

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2. Summary of Earlier Results

Two promising lines of approach were found by CMR-2 in its early work (LA-1215) on direct combination: (1) direct combination in a metal crucible enclosed in a metal reactor, (2) direct combination followed by distillation of the product onto a "cold finger" for easy removal of the product. Although both of these methods may appear quite simple and obvious, there were many experimental difficulties yet to be overcome when the project was reactivated in 1951.

3. Apparatus and Materials

The apparatus was quite simple. It included a rudimentary vacuum system made entirely of metal except for the diffusion pump. The reaction vessels themselves were usually made of stainless steel and were gasketed with soft copper rings. Gasket failures were uncommon. They occurred only when a gasket was re-used. The tops of the vessels were bolted on with Allen screws. Heating was done with resistance furnaces, and temperatures were measured by Chromel-Alumel thermocouples in suitably placed thermocouple wells.

The hydrogen used was ordinary tank hydrogen purified by passing it over uranium turnings at 800°C. Simple Bourdon gauges measured the hydrogen pressure.

For the first dozen or so experiments, A. D. Mackay Chemical Co. lithium metal was used. This contained appreciable amounts of sodium and calcium. Later Maywood Chemical Co. "low sodium" lithium was substituted, with no observable effect on the behavior of the reaction. No analyses were run on these metals, but from their apparent equivalent weights as LiH, the Mackay lithium was probably 99% pure, while the Maywood metal was close to 99.9% pure.

The lithium was prepared in a dry box by wiping the protective coating of oil from the metal and then paring away the layer of nitride that was always present. The bright metal was weighed and placed in the reactor. The reactor, still in the dry box, was closed and removed to the synthesis line.

In general, it is necessary only to heat the hydrogen and lithium to about 700°C. to get the reaction started. Once started, the reaction maintains itself. In fact, if hydrogen is admitted too quickly to the reactor, the reaction is likely to "run away." Consequently, it is important to keep careful watch of the reactor temperature and pressure and to adjust the flow of hydrogen accordingly if the amounts of lithium used are much in excess of 100 g.

4. "Cold Finger" Synthesis

This method was tried first, since in earlier work it had proved virtually impossible to

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remove solidified LiH from small metal crucibles.

The cold rolled steel reaction vessel measured 2.0 in. in diameter and 12 in. long. A "cold finger" 1.0 in. in diameter hung down into the reactor to within 2 in. of the bottom. Approximately 1-g. quantities of lithium were placed in the reactor, which was then evacuated. Somewhat less than 1 atm. of hydrogen was admitted to the reactor, which was then heated to the desired temperature. The results are given in Table I.

Table I

RESULTS OF "COLD FINGER" SYNTHESES

Run No.	Furnace Temp., °C.	Cold Finger Temp., °C.	Duration of Run, hrs.	Product
1	700	$\sim$300	$\sim$3	25 mg. $\sim$50% LiH
2	860	400	$\sim$1/2	40 mg. $\sim$91% LiH
3	1000	500	2	1 g. fused on cold finger 91% LiH
4	900	250	3	130 mg. 85% LiH

It is seen that both yield and quality are low. Because of this, and because other approaches looked promising, this approach was abandoned.

5. "Flush Pot" Method

Another scheme in which the use of metal crucibles was avoided involved an apparatus called, for lack of a better name, the "Flush Pot" (See Fig. 1). In this apparatus a stainless steel reaction vessel was connected through a gravity trap to an ordinary steel chamber. The reaction vessel was heated by an electric furnace, and the steel chamber cooled by a water-cooling coil. When the reaction was completed the products were flushed into the chamber by increasing the hydrogen pressure in the reaction vessel. The products solidified on the floor of the chamber and were easily removed. The LiH produced in this apparatus varied in color from dark brown to yellow. Analyses showed the presence of considerable amounts of chromium, as well as low LiH purity (see Table II).

A number of runs were also made in this apparatus at hydrogen pressures of 50 to 150 p.s.i. to see what effect this variable might have on product quality. No difference from the low pressure runs was observed.

This method could probably be modified to give LiH in satisfactory yields and of good purity. Undoubtedly it would work best for larger scale synthesis, say of 10-lb. batches, because there is appreciable "hold up" in the apparatus. Metallic impurities in the product could be eliminated either by thoroughly conditioning the apparatus, or by the choice of a different metal for construction.

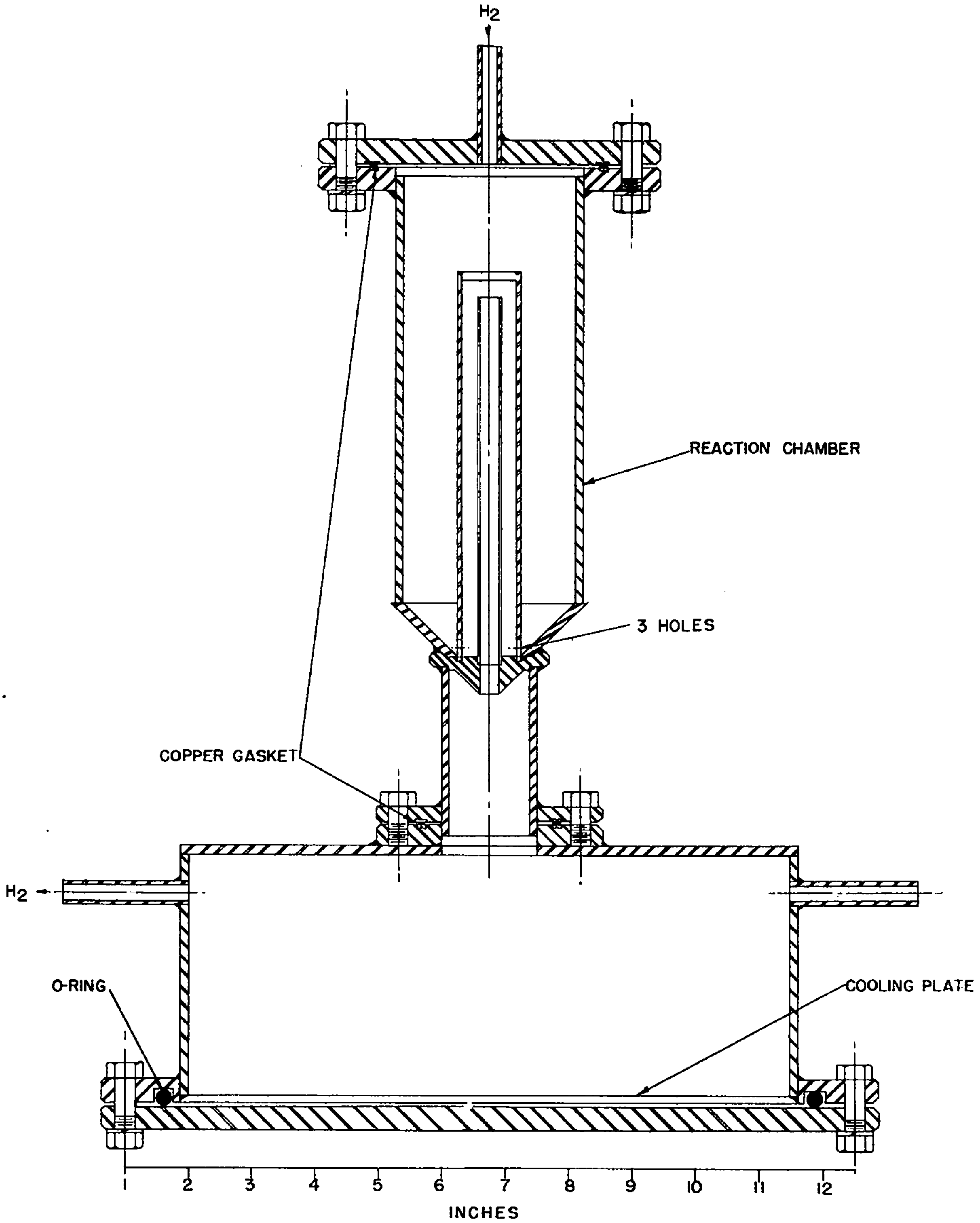

Fig. 1. "Flush Pot" apparatus for preparing lithium hydride.

6. Uranium Crucible Method

The main problem in synthesizing LiH in metal crucibles is the great difficulty encountered in removing the product from the crucible. The few metals (iron, chromium, molybdenum) that neither molten lithium nor molten LiH attack to any great extent stick very strongly to the solidified LiH. It was hoped that by using uranium crucibles this difficulty could be eliminated.

Uranium metal has the property of reacting rapidly with hydrogen below about 400°C. to form a finely powdered hydride, UH_3. Above about 450°C. uranium is inert to hydrogen at low (1 atm.) pressures. The idea was to run the reaction $2Li + H_2 \rightarrow 2LiH$ to completion in a uranium crucible, then let the LiH solidify (680°C.). The reactor was then to be cooled to below 400°C., and more hydrogen run in. This was supposed to react with the uranium crucible, causing it to powder away from the solidified LiH.

After a preliminary experiment was performed in which it was proved that uranium does not react with LiH, several syntheses were run in uranium crucibles. Two runs were made in crucibles 3/4 in. O.D., 1 1/2 in. tall, with 1/32 in. walls. Three runs were made in crucibles 3 in. O.D., 2 - 3 in. tall, deep drawn from 10-mil uranium sheet. The reaction chamber itself was made of stainless steel tubing. The hydriding of the crucible worked beautifully in all cases. The product had a bluish cast and was in the form of large translucent crystals. The yields and purity (see Table II) approached 100%. However, three of the products were analyzed and found to contain 0.02 - 0.03% uranium by weight. This was considered to be too much to be tolerated, so the idea was abandoned.

It was later found that the blue color bears no relation to the presence of uranium, but rather is characteristic of high purity LiH.

7. Metal Crucible Preparations

In spite of the difficulties encountered in their use, synthesis in metal crucibles was studied in detail. This method of synthesis was eventually developed into the most satisfactory procedure for our purposes, with the limitation that batches of at least 50 to 100 g. must be made in order to ensure effective removal of the product from the crucible.

The crucibles used measured roughly 3 in. in diameter and 3 in. deep, suitable for 50 to 100 g. LiH. Metals used for crucible construction were molybdenum, stainless steel, and iron, because of their availability and relative inertness towards lithium and LiH.

Molybdenum crucibles showed considerable promise because, in some cases, the product did not stick to the crucible and could be lifted out easily. However, in other cases, part came out easily and part stuck tenaciously; while in still others, the whole product stuck badly.

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In stainless steel and in iron crucibles, the product always stuck and had to be removed with a hammer and cold chisel. With practice and a little patience, nearly quantitative removal could be effected.

Since molybdenum offered no real advantage, stainless steel crucibles were selected for use in synthesizing LiH on a routine basis. As may be seen in Table II, LiH produced by this method is of very high purity.

It is characteristic of the crucible method that, on cooling, large cavities form in the LiH. This is caused by the nearly 10% contraction in volume that takes place in solidification. Impurities in the melt concentrate in the crystals lining these cavities. These impure crystals can usually be removed with little trouble and the loss of only a small amount of LiH. Even this loss can be minimized by thoroughly conditioning the crucible with long exposure to hot LiH or by repeated re-use. Evidently the first runs condition the crucible by dissolving out most of the substances which contaminate the product. However, a small amount of contamination always occurs at the surface of the LiH that was in contact with the crucible. This can be removed either with a wire brush or by gently wiping the surface with a piece of tissue dampened with absolute alcohol.

Table II

YIELD AND PURITY OF LiH FROM VARIOUS SOURCES

Method or Source	Yield, %	Purity, %	Comments
Uranium crucible	98	99.6	Blue crystals
"Flush Pot"	est. 90	96.3	Brown with light patches
Stainless steel crucible	-	-	(10-1000 p.p.m. Ni, 10-100 p.p.m. Cr, <10 p.p.m. Fe, brown)
Stainless steel crucible	-	99.8	170 p.s.i. H_2, pink, blue, brown
Stainless steel crucible	-	99.9	100 p.s.i. H_2, pink, blue, brown
Molybdenum crucible	-	99.9	Pearly gray blue
Metal Hydrides special Lab. sample*	-	94.3	Almost pure white
Maywood Chem. Co.	-	96.2	Gray
Metalloy Corp.	-	98.6	Gray

*This sample had been accidently contaminated with KBr, hence the relatively low purity. The KBr crystals were clear and colorless and were avoided in selecting material for analysis.

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8. Purity and Color of the Product

Table II gives typical results as to yield and purity* of the LiH made by the methods discussed in this report. Also included are some analytical results obtained from various commercial samples. Commercial Metal Hydrides, Inc., material was not analyzed. The main impurity in the samples is LiOH.

Our experience has been that masses of pure LiH are colored blue or light gray, probably because of lattice deficiencies or fracture planes. It has been reported** that blue LiH may be converted to white LiH by heating it in an atmosphere of hydrogen; and that white LiH will turn blue if heated in vacuo. These observations we have been unable to confirm. The material from the fourth preparation (Table II) was reheated nearly to the melting point under a pressure of 100 p.s.i. of hydrogen, with no change in color. This same material later was reheated in vacuo, again with no change, although metallic lithium was distilled from the sample. Actually, a single thin crystal of pure LiH is quite transparent. These crystals, which are face-centered cubic, are easily cleaved from large lumps of material.

9. LiD and LiT Preparation

Only one preparation of LiD has been made. As might be expected, the run was in all respects similar to the LiH syntheses.

A number of syntheses of LiD-LiT mixtures have also been carried out. The apparatus for these differed from the LiH apparatus slightly. The deuterium-tritium mixtures were supplied from "uranium furnaces."*** The uranium furnaces were stainless steel cylinders about 2 in. in diameter and 20 in. high, provided with high pressure valves. These cylinders contained uranium deuteride-tritide, from which the gases could be released by heating to about 450°C.

The LiD-LiT syntheses were complicated by one factor. During the runs, enough He^3 collected in the system to slow down diffusion of the gas to the molten lithium. Also, at the conclusion of the runs, the accumulated He^3 blocked reabsorption of the excess deuterium-tritium by the uranium furnace. The net effect was that the total time for these syntheses was considerably longer than for LiH. Six to eight hours was required instead of two to three. Redesign of the vacuum line would easily eliminate this annoyance.

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* The LiH was analyzed by the methods outlined August 1952 by G. E. Challenger, H. D. Cowan, and J. F. Lemons in LAMS-1547 (report not available).

** Albert and Mahe, loc. cit. They believe the blue color is caused by excess lithium.

***The charged furnaces were supplied by B. B. McInteer and R. M. Potter of Group CMR-4, LASL.

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Table III gives the yield and composition for these LiD-LiT syntheses.

Table III

LiD-LiT SYNTHESES

Run No.	Composition	Yield, %	Wt., g.	
CH-LiT-2	95% LiH - 5% LiT	100	20.1	Product very black and shiny.
CH-LiT-3	50% LiT-50% LiD	99	26.1	Product black and shiny; actual composition 48.7% LiT, 49.2% LiD.
CH-LiT-4	50% LiT-50% LiD	100	44.7	Product same as above; actual composition 48.1% LiT, 49.2% LiD.

The purity in all cases was 100%, within the limit of accuracy of the analytical method.*

Note in the table that LiD-LiT is black (although thin pieces are translucent) instead of gray or blue. It is also much more brittle than LiH, which facilitates removal of the product from the synthesis crucibles. This brittleness increases with the passage of time, so that after several months large lumps of LiD (60%) - LiT (40%) disintegrate spontaneously to small crystals. A discussion of this and other radiation induced phenomena is beyond the scope of this report.

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*LAMS-1547, pages 8-10, reports LiD-LiT analytical procedures. (Not available.)

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