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May 26, 1933

Benjamin M. Walker

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A thesis, presented to the Department of Chemistry of Union College, in partial fulfillment of the requirements for the Degree of Bachelor of Science in Chemistry by

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Approved by

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INTRODUCTION

Much work has been done on the study of the hydrides of the alkali metals and the alkali earth metals. Calcium hydride, in particular, has been the subject of extensive study. The method in general is to measure the equilibrium pressure of hydrogen at a definite temperature. In the equilibrium between metal, metal hydride, and hydrogen, hydrogen is the only gaseous constituent if the temperature is not too high, and its equilibrium pressure is a measure of the reaction constant K_p .

In previous work at the Union College laboratory¹¹, a method was finally developed which overcame the difficulties of the earlier studies of this calcium-hydrogen equilibrium. The results obtained were in good agreement with the best work of other investigators. In the present work, an attempt was made to extend this method to a study of the lithium-hydrogen equilibrium.

HISTORICAL

In 1874, P. Hautefeuille and L. Troost¹ found that lithium, sodium, and potassium absorb hydrogen without changing their metallic appearance as does palladium.

In 1900, C. Matignon² found that if lithium, in an iron boat, is heated to redness in a stream of hydrogen, the metal burns with incandescence forming a hard mass of lithium hydride.

In 1896, A. Guntz³ prepared lithium hydride from lithium nitride in a stream of hydrogen and a mixture of lithium hydride and carbide by heating lithium in a stream of acetylene. Lithium hydride so prepared is a hard white mass which melts at 680° C. at which temperature the dissociation pressure is 27 mm. The empirical composition corresponds with LiH.

Vapor pressures of lithium were given by A. Kroner⁴ in 1913 as follows:

630°	731°	765°	799°	867°	900°	1000° C.
.05	.60	1.0	1.7	3.7	5.5	760 mm.

It is to be noted that at temperatures of 500-600° the vapor pressure of lithium is very small.

In 1920, K. Moers⁵ found the heat of formation of lithium hydride ($\text{Li}, \frac{1}{2}\text{H}_2$) to be = 21.6 ± .250 Cal.

In 1923, A. Guntz and F. Benoit⁶ determined the heat of formation of lithium hydride as 43.6 Cal.

In 1921, F. Ephraim and E. Michel⁷ said that the reaction of hydrogen and lithium is very violent and

is completed rapidly. The resulting compound is very stable. On heating the hydride, the partial removable of hydrogen causes a large rise in temperature. Formation of the hydride begins before the metal is fused and the smooth reaction is probably due to the great solubility of the metal in the hydride.

No references were found for work done on the thermal dissociation of lithium hydride.

The method used in the present work was developed in a study of calcium hydride.

In 1923, Kraus and Hurd⁸ heated the calcium hydride in a vertical iron cylinder with the lower end closed and the upper end open in a quartz tube and measured the equilibrium pressures of hydrogen at various temperatures. The object of the iron cylinder was to protect the quartz tube from chemical action with the calcium hydride. Some calcium did get out, however, and there was some blackening of the quartz tube near the mouth of the iron cylinder.

In 1929, Kassner and Stempel⁹ used the same method using an open iron tube and showed by experiment that the amount of solid lost out of the equilibrium was negligible in their experiments.

The next improvement to be made in this study was the use of sealed metal cylinders which were permeable to hydrogen at the temperature of the experiment but not to calcium or calcium hydride.

In work at Union College¹¹, sealed iron cylinders were tried but abandoned because consistent results could not be obtained.

In 1929, Remy-Cennete¹⁰ published the results of his work in which he used an iron cylinder with a sheet of iron welded over one end.

In 1931, Hurd and Walker¹¹ published the results of their work at Union College in which they used a nickel cylinder which was sealed with nickel plugs pounded in the ends. The results of their work are consistent and in good agreement with the results of Remy-Cennete¹⁰.

APPARATUS AND PROCEDURE

The apparatus used was the same as that described by Hurd and Walker¹¹. A diagram of the system is shown in Figure 1.

A nickel cylinder about 4" long was prepared with tightly fitting nickel plugs, all turned on a lathe. One plug was hammered tightly into place. The cylinder was then filled with pure lithium metal. The lithium was scraped clean and placed in the cylinder, all being done in an atmosphere of hydrogen. This was done in a hydrogen bottle at the General Electric Co. Research Laboratory. The other nickel plug was then put in place and hammered tight. The nickel cylinder and plugs were weighed before and

after filling so that the amount of lithium used was known.

The cylinder was placed near the closed end of a long quartz tube and the tube was supported horizontally in the electric furnace. The quartz tube was sealed to the vacuum system with a de Khotinski cement joint. The system was evacuated and the cylinder was heated to 200-300°C. to drive out the absorbed gases.

Hydrogen could then have been let into the system, and it would penetrate the nickel cylinder and react with the lithium forming lithium hydride, because nickel is porous to hydrogen if the temperature is high enough. All pressure measurements were shown by a mercury manometer measured with a cathetometer which was accurate within .01 cm.

An Alumel-Chromel thermocouple was calibrated at the Lead, Aluminum, and Copper points to be used for temperature measurements. The calibration agreed as accurately as could be determined with the manufacturer's calibration curve, the measured potentials at each of these temperatures agreeing within .0001 volts. The manufacturer's curve was therefore redrawn on a larger scale and used as a calibration curve.

The electric furnace was run on a 220 volt circuit. The temperature could be kept quite constant by keeping the current through the furnace constant. The current was kept constant in spite of line voltage variations of as much as 40 volts

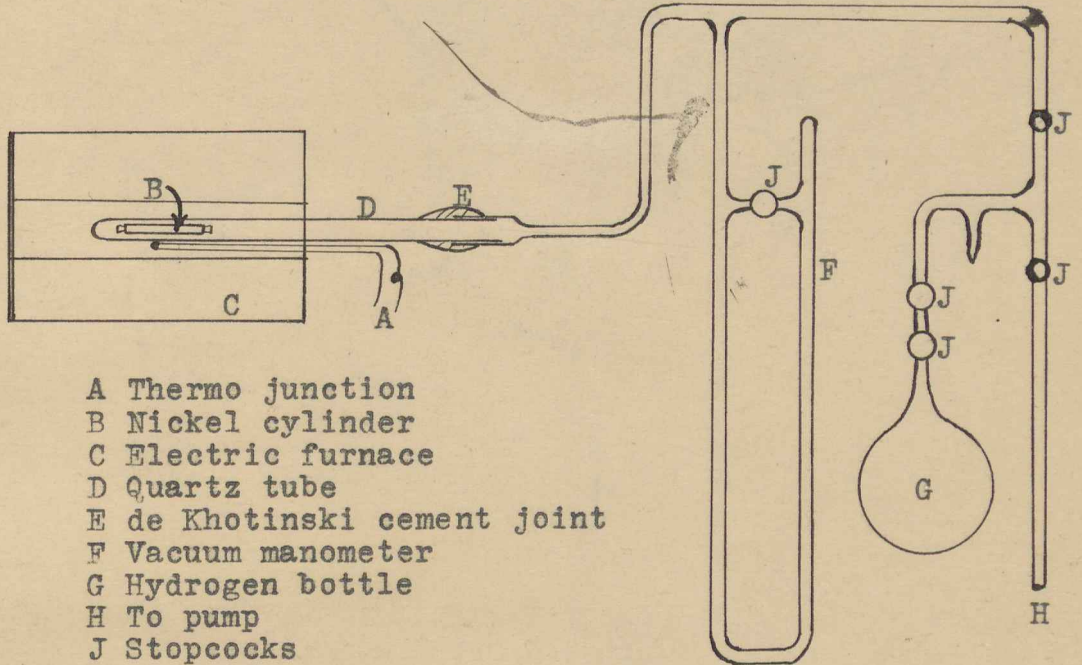
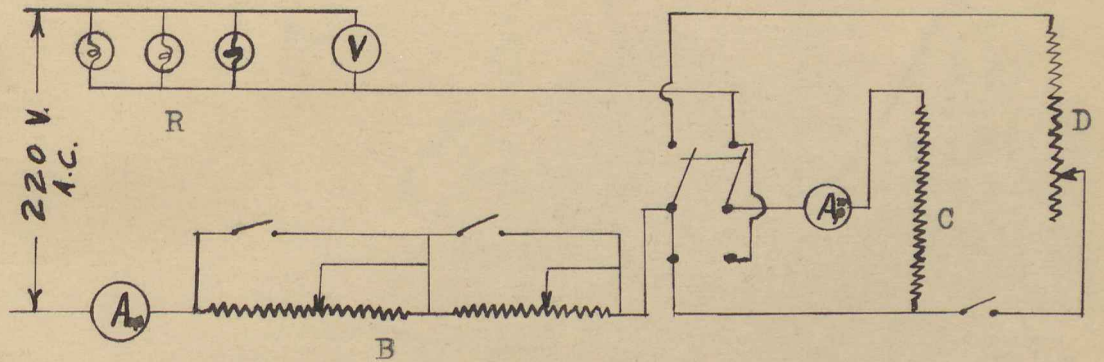
FIGURE 1FIGURE 2

FIGURE 3

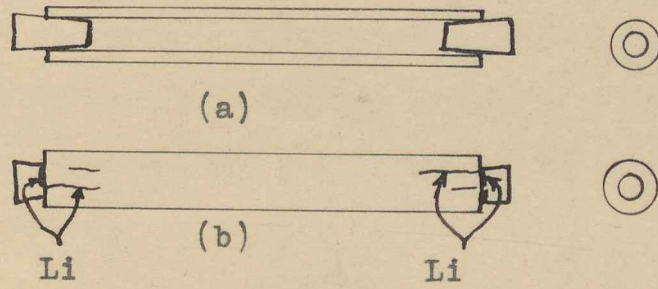
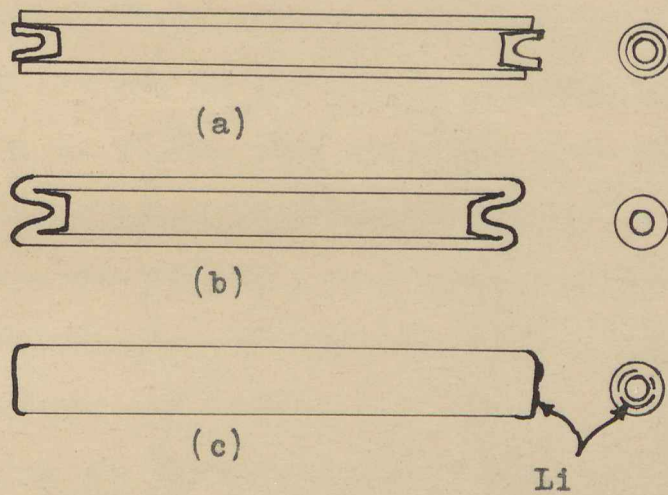


FIGURE 4



by using one, two, or three UV-876 ballast tubes in parallel connected in series with the circuit. Each combination of tubes passed a constant current of a definite amount. A variable resistance shunted across the furnace allowed any fraction of this constant current to pass through the furnace. The circuit used is shown in Figure 2.

RESULTS

This work never progressed much beyond the stage of heating the nickel cylinder to drive out absorbed gases, because it was found to be impossible to keep the lithium in the nickel cylinder at temperatures of 500°C . Four cylinders were tried. Two of these cylinders had been prepared, filled with lithium, and sealed a year and a half before this work was started and two others were prepared after the others had failed.

The first two cylinders were heated to 300°C . and after two or three such heatings, the temperature was raised to 500°C . preparatory to introducing hydrogen into the system. The lithium came through the cylinders around the edges of the plugs and also through what appeared to be small cracks in the nickel cylinder where the plugs had been hammered in. (Figure 3). In one of the other cylinders lithium came through as it had with the first two. In the fourth cylinder, no cracks were found after three

heatings to $400^{\circ}\text{C}.$, but the lithium still came through around the edges of the plugs. The plugs in this cylinder were pounded in harder, and the cylinder was reheated but the result was the same as before.

It was suspected that the lithium metal attacks the nickel cylinder at the temperature used, and that the trouble was not with the plug joints which were used. A cylinder was therefore fitted with plugs with flared edges which fitted flush with the end of the nickel cylinder (See Figure 4a). These plugs were not hammered in place as was previously done. They were firmly tapped into place and then arc-welded closed in an atmosphere of hydrogen. This made a very tight seal (See Figure 4b). After two heatings to $500^{\circ}\text{C}.$, however, lithium came through the nickel cylinder where the weld had been made. The walls of the tube were thinnest at the weld. The vapor pressure of lithium at a temperature of $500^{\circ}\text{C}.$ is less than $.05 \text{ mm.}^4$ and is not therefore excessively high. This would seem to show definitely that lithium attacks the nickel and that no seal can be made strong enough for a nickel cylinder to hold lithium metal at a temperature of $500^{\circ}\text{C}.$

CONCLUSIONS

It would seem that the method used in studying the thermal dissociation of calcium hydride is impossible of application to a study of the dissociation of lithium hydride. Lithium is so active chemically at the temperatures used that nickel cylinders will not contain it. The lithium works its way through the nickel cylinder and condenses on the cooler parts of the quartz tube.

It is possible that cobalt cylinders could be used in place of nickel cylinders in the study of lithium hydride. It is also quite possible that the nickel cylinders could be used in a study of barium or strontium hydrides.

This result illustrates the fact that the metal cylinder must not only be permeable to hydrogen and not to the other constituents but must also be not attacked by the metal contained.

BIBLIOGRAPHY

- (1) P. Hautefeuille and L. Troost
 Ann. Chim. Phys., (5), 2, 273 (1874)
 Compt. Rend., 78, 809 (1874)
- (2) C. Matignon Compt. Rend., 131, 891 (1900)
- (3) A. Guntz Compt. Rend., 122, 244 (1896)
123, 694, 995, 1273 (1896)
- (4) A. Kroner Ueber die Dampfdrucke der Alkalimetalle,
 Leipzig, (1913)
- (5) K. Meers Zeit. anorg. Chem., 113, 179 (1920)
- (6) A. Guntz and F. Benoit
 Ann. Chim., 20, 5-33 (1923)
- (7) F. Ephraim and E. Michel
 Helvetica Chim. Acta., 4, 900-24 (1921)
- (8) Kraus and Hurd J.A.C.S. 45, 2559 (1923)
- (9) Kassner and Stempel
 Zts. anorg. allgem. Chem., 181, 83 (1929)
- (10) Remy-Cennete Compt. Rend., 189, 579-81 (1929)
- (11) Hurd and Walker Thesis, Union College (1930)
 J.A.C.S. 53, 1681 (1931)