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The Solid-State Reaction of Lithium Hydride and Aluminum[1a]

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The compound LiH is fairly stable in inert atmospheres, having a melting point of 688°[2] and a vapor pressure of hydrogen of approximately 2 mm at 600°.[2] A number of investigators[3-6] have studied the decomposition of $LiAlH_4$. The decomposition is complex and occurs in a number of stages. It was suggested that the last stage involves the decomposition of LiH to form lithium metal and hydrogen.[6] It was observed, however, that the hydrogen in this last stage was rapidly released well below 600°.[4-6] This rapid decomposition at a relatively low temperature suggests the possibility that the release of hydrogen resulted from a reaction between LiH and Al rather than from the decomposition of LiH itself.

It was, therefore, of interest to determine if a reversible reaction between LiH and aluminum occurs in the solid state and if thermodynamic information in the Li–Al–H system could be obtained. The reaction of LiH and Al was studied at temperatures of 450–550° using two starting materials: (a) an admixture of LiH powder and aluminum powder and (b) the product which results when $LiAlH_4$ is decomposed at 230°.

Experimental Section

Chemicals.—$LiAlH_4$ powder was obtained from Metal Hydrides, Inc., Beverly, Mass. The powder was specified to be more than 95% pure. LiH powder was obtained from the Lithium Corp. of America, Bessemer City, N. C. The aluminum powder was supplied by the Atlantic Powdered Metals Co., New York, N. Y. The major metallic impurities observed by spectrographic analysis, in weight per cent, were: 1.0% Fe, 0.5% Si, 0.1% Cr, and 0.1% Ni in the aluminum sample; 0.3% Fe, 0.3% Si, 0.3% Al, and 0.3% Ca in the LiH sample; 0.07% Si and 0.02% Fe in the $LiAlH_4$ sample. All grinding and mixing of powders was done in an inert atmosphere in a mixer-mill obtained from Spex Industries, Metuchen, N. J.

Procedure.—The reaction mixture was put in a porcelain crucible and was placed inside a quartz tube which was then connected to a vacuum system.[7] Two chromel–alumel thermocouples were attached to the quartz tube adjacent to the sample. One was used for temperature control and the other for temperature measurement. A tube furnace was placed around the sample. The pressures of hydrogen in the system were measured with a mercury manometer. The approximate volume of the system was 500 cm^3. X-Ray diffraction data on the reactants and reaction products were obtained using standard powder techniques.

Results and Discussion

Pressures of hydrogen over the powders were measured at 450–550°. Each sample was heated *in vacuo* at 315° to remove adsorbed gases. Two typical plots of hydrogen pressure *vs.* temperature are shown in Figure 1. Approximately 1 hr was required at each temperature to attain equilibrium. Data obtained after increasing or decreasing the temperature were the same. Several temperature cycles were made on each sample. The data in each cycle were similar. The reaction was reversible and may be written

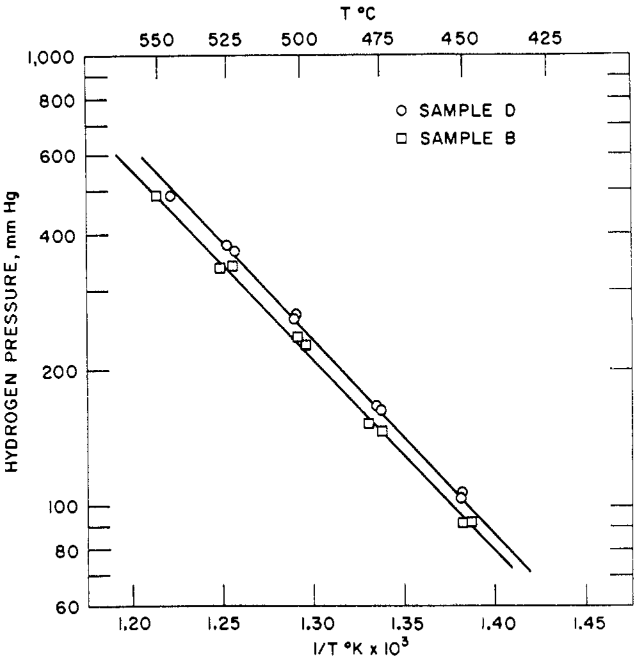

Figure 1.—The temperature dependence of the vapor pressure of hydrogen.

$$2\mathrm{LiH(s)} + 2[\mathrm{Al(s)}] = 2[\mathrm{LiAl(s)}] + \mathrm{H_2(g)} \qquad (1)$$

Brackets are placed around the Al and LiAl phases to indicate that these are not pure stoichiometric phases but represent compositions at the phase boundaries. The solubility of lithium in aluminum is 9 atom % at 450° and increases to 12 atom % at 550°.[8,9] [Al(s)], therefore, represents aluminum with about 10 atom % dissolved lithium. The aluminum-rich phase boundary of the LiAl phase occurs at 45 atom % lithium at 450–550°.[8] This composition is represented by [LiAl(s)]. Since equilibrium in the lithium–aluminum system occurs fairly rapidly at 450–550° and steady pressures were obtained in this study after about 0.5 hr at each temperature, it is likely that equilibrium conditions prevailed and that reaction 1 represents the reaction occurring in all of the samples investigated.

X-Ray diffraction data were obtained on a number of samples of the reactant mixture and of the reaction

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(1) (a) This work was performed under the auspices of the U. S. Atomic Energy Commission. (b) Department of Chemistry, Brooklyn College, City University of New York, Brooklyn, N. Y.

(2) C. E. Messer and T. R. P. Gibb, Jr., AEC Report NYO-8022, "A Survey Report on Lithium Hydride: Supplement 1954–57," Aug 1957.

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(6) M. McCarty, Jr., J. N. Maycock, and V. R. Pai Verneker, *J. Phys. Chem.*, **72**, 4009 (1968).

(7) Some attack on the porcelain crucible by the reaction mixture was observed after a run. The crucible was blackened but not cracked or pitted. One crucible was used for several runs.

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product. In the latter case, reaction 1 was pushed to completion by removing the hydrogen from the system. The LiAl phase was the only product observed. In both the partial decomposition product of $LiAlH_4$ and the admixture, the X-ray pattern for aluminum was observed but not that for LiH. A possible reason for the absence of the LiH pattern is the low diffracting power of the atoms in LiH resulting from their low atomic numbers. In the presence of aluminum, which absorbs part of the X-ray beam, the LiH lines may be too weak to observe.

It is observed in Figure 1 that a plot of log (pressure) *vs.* reciprocal temperature is linear. The following standard equation can, therefore, be used to obtain thermodynamic information on reaction 1

$$\ln P = (\Delta S/R) - (\Delta H/RT) \qquad (2)$$

The thermodynamic data obtained on each sample are summarized in Table I. Similar data were obtained on admixtures of LiH and Al and on the partial decomposition product of $LiAlH_4$. The heat absorbed in reaction 1 is 19.2 ± 1 kcal/mol of H_2. The entropy change in the reaction is 28.6 ± 1 cal/deg mol of H_2. The large positive entropy change results primarily from the production of hydrogen gas.

TABLE I
HEAT AND ENTROPY CHANGES FOR REACTION 1
CALCULATED FROM THE EXPERIMENTAL DATA

Sample designation	Initial composition	ΔH, kcal/mol of H_2	ΔS, cal/deg mol of H_2
A	0.46 g of LiH + 1.54 g of Al	19.4	28.7
B	0.35 g of LiH + 1.16 g of Al	19.5	29.2
C	0.23 g of LiH + 0.77 g of Al	18.6	27.6
D	0.26 g of LiH + 1.74 g of Al	19.7	29.2
E	2.00 g of $LiAlH_4$	19.0	28.4
F	1.50 g of $LiAlH_4$	19.2	28.8
G	1.17 g of $LiAlH_4$ + 0.83 g of Al	18.8	28.1

Information on the heat of formation of the LiAl phase can be obtained from the data. For this purpose, it is useful to rewrite reaction 1 in terms of the atomic compositions of the phases.[8,9]

$$2LiH + 3.14Al_{0.90}Li_{0.10} = 2.57Al_{1.10}Li_{0.90} + H_2 \qquad (1')$$

The heat of formation of LiH at about 500° can be calculated from its known heat of formation at 298°, −21.50 ± 0.5 kcal/g-atom of Li. This is the average of two measured values.[10,11] The heat of formation of LiH at 500° from liquid lithium and gaseous hydrogen is calculated to be −22.1 ± 1 kcal/g-atom of Li using specific heat data on LiH,[12,13] Li,[14] and hydrogen[14] and the heat of fusion of Li.[14] Using this value in reaction 1′, the heat of the reaction

$$1.57Al_{0.90}Li_{0.10}(s) + Li(l) = 1.29Al_{1.10}Li_{0.90} \qquad (3)$$

at about 500° is −12.6 ± 1 kcal/g-atom of Li. The reported heat of formation of LiAl,[15] −13.0 ± 4 kcal/g-atom of Li at 298°, is in good agreement with this value. It is also similar to the heats of formation of LiPb, LiCd, LiTl, and LiSn[15] which are, respectively, −14.6, −12.0, −12.8, and −16.8 kcal/g-atom of Li, respectively.

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Studies on the "Isomeric" Forms of Some β-Diketone Complexes of Europium(III) and Neodymium(III)[1]

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The coordination chemistry of rare earth elements has been investigated by a large number of researchers and extensive reviews have been published.[3–5] One important result of this work was the discovery that certain complexes of europium(III) are promising as laser materials.[6] Two compounds whose fluorescence spectra have received considerable attention[7–10] and which have shown laser action in alcohol solution are piperidinium tetrakis(1,3-diphenyl-1,3-propanediono)europate(III) and piperidinium tetrakis(1-phenyl-1,3-butanediono)europate(III). The anionic ligand moieties are also called dibenzoylmethanate and benzoylacetonate and the compounds are abbreviated as $[Pip][Eu(DBM)_4]$ and $[Pip][Eu(BA)_4]$, respectively.

Bauer, Blanc, and Ross[8] reported these two compounds and the Gd analog with DBM each to have two

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[2] Summer Research Participant at Oak Ridge National Laboratory.

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