Lithium Hydride Systems: Solid-Liquid Phase Equilibria for the Ternary Lithium Hydride–Lithium Chloride–Lithium Iodide System

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Thermal analysis has been used to determine the solid-liquid phase diagram for the lithium hydride–lithium chloride–lithium iodide ternary mixture. The three binary mixtures—LiH–LiCl, LiH–LiI, and LiCl–LiI—which make up this ternary system are all eutectic in nature. The diagram of the crystallization surface consists of three areas, one for each of the pure components in the system. At the intersection of these three fields lies the minimum in the system, a ternary eutectic of 15.3° m/o LiH–27.3 m/o LiCl–57.4 m/o LiI melting at 333.2° C.

THE THERMALLY regenerative ionic hydride cell has the potential of serving both as an energy conversion device and as an energy storage device. For optimization as a regenerative cell, it is desirable to operate the cell portion of the device at low temperatures in order to maximize the Carnot cycle efficiency. Thus, low-melting electrolyte systems are desired. Further, these electrolyte systems should have reasonable solubility for lithium hydride, and should be thermodynamically stable with respect to the very electropositive lithium metal. This paper reports a continuation of previous studies on such electrolyte systems (*3*). Liquid-solid phase equilibrium data are given for the LiCl–LiI binary mixture and the LiH–LiCl–LiI ternary mixture.

EXPERIMENTAL

All operations were performed in an inert atmosphere box filled with helium having an impurity content of 0.5 p.p.m. H_2O and less than a total of 5 p.p.m. O_2 and N_2 (*2*). The thermal analysis apparatus has been described in detail (*4*). A minimum pressure of 1 atm. of hydrogen was maintained in the thermal analysis apparatus during the experimental work on LiH–LiCl–LiI ternary mixtures.

Reagent grade lithium chloride (J. T. Baker Chemical Co.) was purified with chlorine gas, using the method of Maricle and Hume (*7*). The melting point was 606.8° C. Reagent grade lithium iodide ($LiI \cdot 3H_2O$) (Mallinckrodt Chemical Co.) was purified, using a modification of the procedure described by Laitinen *et al.* (*6*), in which anhydrous hydrogen iodide was used to remove the last traces of moisture from the molten salt. Preceding the treatment with anhydrous hydrogen iodide, the bulk of the water of hydration was removed from the finely ground crystals by vacuum during slow programmed heating of the lithium iodide. The lithium iodide melting point was 469.2° C. Lithium hydride was prepared by bringing high-purity liquid lithium metal (99.99% Li) in contact with purified hydrogen at 750° C. (*4*). Commercial hydrogen gas was purified before use by passage through a silver palladium alloy held at 400° C. The lithium hydride melting point under 1 atm. of hydrogen was 686.4° C.

Temperatures were sensed with a Pt/Pt-10% Rh thermocouple which had been calibrated against NBS pure Zn (m.p. 419.5° C.) and NBS pure Al (m.p. 660.0° C.). The accuracy of the temperature measurements was estimated to be ±0.3° C.

The amounts of the pure components required for a given composition were weighed into a sample capsule. After being placed in the thermal analysis assembly, the sample was heated to a temperature high enough to ensure complete melting, and was maintained in the liquid state for one hour. Preliminary cooling and heating cycles were then executed until reproducible first breaks were obtained in the cooling curves. Only then were complete cooling and heating curves recorded. Cooling rates were set in the range of 0.5° to 1° C. per minute, thereby maintaining close control of the heat flow into and out of the system. The sample composition was calculated from the weights of the pure materials; however, periodic checks were made by chemical analysis on selected samples.

DISCUSSION

Temperature-composition data for the LiCl–LiI system were obtained over the composition range 5 to 95 mole % LiI (Table I and Figure 1). A eutectic composition of 34.6 mole % lithium chloride in lithium iodide, melting at 368.2° C. was observed. The eutectic melting point was constant (±1.5° C.) across the experimentally measured portion of the diagram. Formation of solid solutions was not observed for mixtures from 5 to 95 mole % in either thermal analysis (based on the persistence of the thermal effect for the eutectic over this concentration range) or in x-ray diffraction analysis of the solid phases.

The LiH–LiCl and LiH–LiI binary mixtures were investigated by Johnson, Wood and Crouthamel (*4, 5*). Both mixtures are eutectic in nature, the LiH–LiCl binary having a eutectic composition of 34.0 mole % LiH melting at 495.6° C. and the LiH–LiI binary having a eutectic composition at 29.7 mole % LiH melting at 390.8° C. The LiCl–

Table I. Crystallization Temperatures for the LiCl–LiI and LiCl–LiH Systems

LiCl–LiI			LiCl–LiH		
Composition, mole fraction LiI	Temp., ° C. Liquidus	Solidus	Composition, mole fraction LiH	Temp., ° C. Liquidus	Solidus
0.000	606.8		0.000	606.8	
0.050	592.4	367.6	0.150	562.4	496.2
0.150	560.7	367.9	0.250	532.1	496.7
0.250	532.0	368.7	0.340	495.6	495.6
0.350	498.9	369.3	0.400	518.8	495.3
0.450	461.6	369.4	0.450	536.8	496.5
0.550	421.9	369.1	0.500	561.5	495.8
0.600	395.7	369.0	0.550	568.5	495.8
0.635	379.1	368.7	0.600	584.4	496.0
0.654	368.2	368.2	0.650	598.7	495.2
0.700	388.2	367.7	0.700	610.8	495.3
0.749	399.3	367.8	0.800	636.3	494.7
0.800	414.7	368.0	0.940	670.3	495.0
0.900	442.3	366.7	0.990	683.7	494.5
0.949	456.1	367.5	1.000		
1.000	468.9				

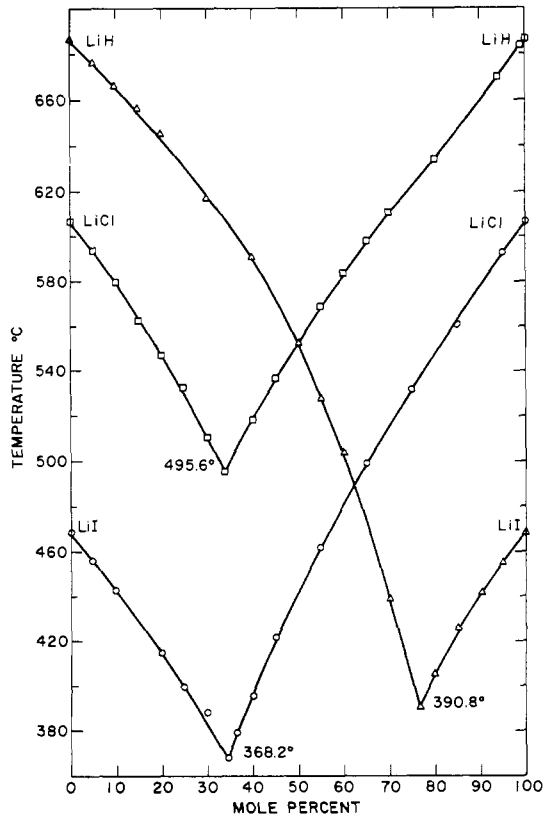

Figure 1. LiCl–LiI, LiH–LiCl, LiH–LiI binary systems

Table II. Crystallization Temperatures for LiH–LiCl–LiI System

Series I Mole Ratio LiCl:LiI 9:1		Series II Mole Ratio LiCl:LiI 7:3		Series III Mole Ratio LiCl:LiI 1:1	
LiH mole fraction	Temp., °C.	LiH mole fraction	Temp., °C.	LiH mole fraction	Temp., °C.
0.000	577.2	0.000	515.8	0.000	443.3
0.100	545.8	0.100	488.7	0.050	430.2
0.150	534.3	0.150	477.2	0.100	420.4
0.200	524.3	0.200	464.6	0.150	412.9
0.300	485.2	0.300	460.0	0.201	404.0
0.400	518.4	0.350	495.2	0.251	433.5
0.500	559.4	0.400	515.7	0.350	489.0
0.600	587.8	0.500	552.8	0.450	534.5
0.700	612.5	0.600	588.5	0.550	578.5
0.750	625.6	0.700	614.2	0.650	609.4
0.850	647.3	0.800	637.2	0.750	629.5
0.896	657.3	0.894	660.4	0.850	650.4
0.950	675.0	1.000	686.4	0.950	674.3
1.000	686.4			1.000	686.4

Series IV Mole Ratio LiCl:LiI 3:7		Series V Mole Ratio LiCl:LiI 1:9		Series VI Mole Ratio LiH:LiCl 34:66	
LiH mole fraction	Temp., °C.	LiH mole fraction	Temp., °C.	LiI mole fraction	Temp., °C.
0.000	384.8	0.000	442.3	0.000	495.6
0.050	367.4	0.100	411.1	0.220	445.2
0.100	352.7	0.150	397.8	0.300	428.1
0.150	339.4	0.200	379.6	0.400	403.2
0.200	367.0	0.250	415.9	0.500	363.0
0.250	419.1	0.300	442.7	0.547	343.2
0.300	451.9	0.350	475.9	0.560	340.1
0.400	509.7	0.450	532.1	0.650	360.8
0.500	556.8	0.550	564.4	0.771	400.2
0.600	590.5	0.650	609.3	0.900	440.8
0.700	620.1	0.750	633.1	1.000	469.2
0.800	639.6	0.850	654.1		
0.900	663.2	0.950	676.2		
1.000	686.4	1.000	686.4		

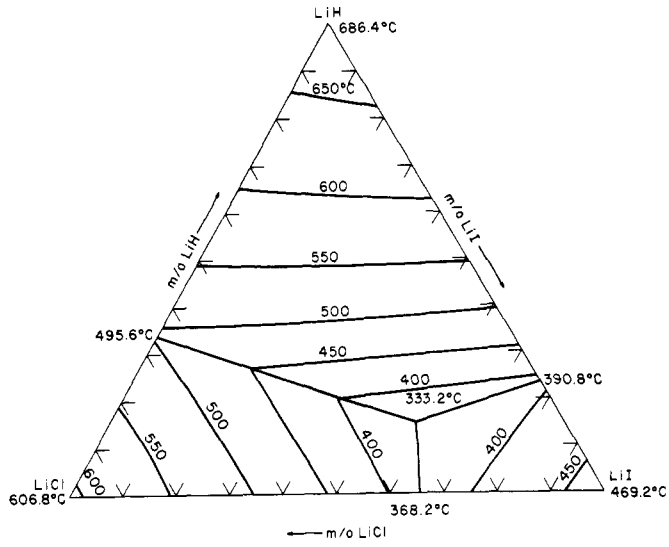

Figure 2. LiH–LiCl–LiI ternary system

LiH system was reinvestigated during this work (Table I and Figure 1), as inconsistencies were noted between the existing binary data (*4*) and the pseudobinary data as given in series I (LiCl-to-LiI mole ratio, 9 to 1). The new data are somewhat lower in temperature for the hydride-rich portion of the binary than were previously reported. The reasons for this difference are not apparent. Some difficulties were encountered at the time the original work was done (*1*), and consistent checks were obtained at that time. Reexamination of the LiH–LiI binary system did not disclose any changes.

To dilineate the crystallization surface in the LiH–LiCl–LiI ternary mixture, six internal sections were investigated. Liquidus-solidus temperature data for differing LiCl-to-LiI mole ratios radiating from the lithium hydride corner of the diagram are given as series I to V in Table II. In addition, a partial cross-section for the pseudobinary system (series VI) of LiH–LiCl eutectic plus pure lithium iodide was studied in order to define more fully the minimum in the system. A contour diagram of the liquidus surface was constructed from the pseudobinary data of systems I to VI (Figure 2). Inspection of the crystallization surface indicates three principle fields, one for each of the pure components LiH, LiCl, and LiI. The intersection of these three fields is the minimum temperature in the system, a ternary eutectic of 15.3 m/o LiH–27.3 m/o LiCl–57.4 m/o LiI melting at 333.2° C.

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