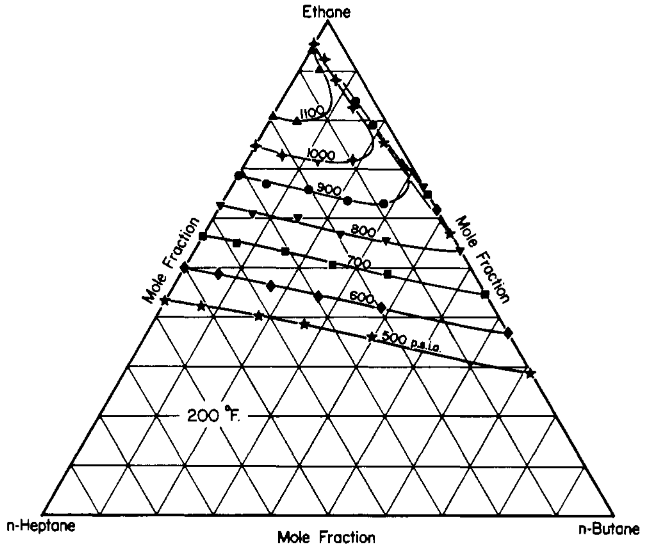

Figure 6. Vapor-liquid equilibrium behavior for ethane–*n*-butane–*n*-heptane system at 200° F.

established as the pressure at which the curves for the three components converged at $K = 1.00$ in a plot of equilibrium constant *vs.* pressure. The resulting critical pressures are plotted against the corresponding compositions of each charge to produce, for each temperature, the relationships presented in Figure 1. The critical pressures of the charges and corresponding binaries were also plotted against the composition parameter, C, to obtain a single relationship for each temperature as shown in Figure 2. The binary data for the systems, ethane–*n*-butane and ethane–*n*-heptane presented by Mehra and Thodos (*8,9*) have been used.

Vapor-liquid equilibrium constants obtained from the smoothed curves of each charge were plotted against the composition parameter for convenient pressures and cross-plotted as K against pressure for constant composition parameters. The resulting curves are presented in Figures 3, 4, and 5 for 150°, 200°, and 250° F., respectively. Final K values for this ternary system obtained from Figures 3, 4, and 5 are presented in Tables IV, V, and VI for 150°, 200°, and 250° F., respectively.

The vapor-liquid equilibrium behavior of this system can be presented in the form of triangular plots as shown for 200° F. in Figure 6. This figure presents the dew point and bubble point curves at 200° F. for convenient pressures and permits the establishment of the two-phase region for pressures above 500 p.s.i.a.

ACKNOWLEDGMENT

The authors express their appreciation to the Phillips Petroleum Co. for the hydrocarbons used in this study and to the National Science Foundation for Grant No. NSF-G9700, which supported this investigation.

NOMENCLATURE

C = composition parameter, $x_i/(x_i + x_h)$
K = vapor-liquid equilibrium constant, y/x
x = mole fraction of a component in liquid phase
x_h = mole fraction in liquid phase of component of lowest volatility
x_i = mole fraction in liquid phase of component of intermediate volatility
y = mole fraction of a compnent in vapor phase

LITERATURE CITED

(1) Carter, R.T., Sage, B.H., Lacey, W.N., Am. Inst. Mining Met. Engrs., Tech. Publ. **1250** (November 1940).
(2) Grieves, R.B., Thodos, George, *Ind. Eng. Chem., Fundamentals* 1, 45 (1962).
(3) Herlihy, J.C., Thodos, George, J. CHEM. ENG. DATA **7**, 348 (1962).
(4) Kay, W.B., *Ind. Eng. Chem.* **30**, 459 (1938).
(5) *Ibid.*,**32**, 353 (1940).
(6) *Ibid.*,**33**, 590 (1941).
(7) Mehra, V.S., Thodos, George, J. CHEM. ENG. DATA **8**, 1 (1963).
(8) *Ibid.*, **10**, 211 (1965).
(9) *Ibid.*,p. 307.
(10) Rigas, T.J., Mason, D.F., Thodos, George, *Ind, Eng. Chem.* **50**, 1297 (1958).

RECEIVED for review January 31, 1966. Accepted March 31, 1966.

Lithium Hydride Systems

Solid-Liquid Phase Equilibria for the Ternary Lithium Hydride–Lithium Chloride–Lithium Fluoride System

CARL E. JOHNSON, ELLEN HATHAWAY, and CARL E. CROUTHAMEL
Argonne National Laboratory, Argonne, Ill.

THE phase equilibrium relationship among the hydride, chloride, and fluoride of lithium metal has been studied. This fused salt system is of interest because of its potential application as the electrolyte in the lithium hydride regenerative galvanic cell. Two of the lateral sides of this ternary system are simple eutectics with no apparent solid solution formation (LiF-LiCl and LiCl-LiH), while the third (LiH-LiF) consists of a complete series of solid solutions. The diagram of the crystallization surface consists of two areas, one comprising mainly a crystallization field of solid solutions continuous between LiH and LiF, with an undetermined possible LiCl content, and a smaller field of pure lithium chloride.

EXPERIMENTAL

The data to determine the crystalline surface were obtained by thermal analysis techniques; the compositions of the solid solutions in equilibrium with the liquid were not determined. The apparatus used has been described in detail (*4*). All experiments were run under a hydrogen pressure of 1 atm.

Reagent grade lithium chloride and lithium fluoride were obtained from J. T. Baker Chemical Co., Phillipsburg, N. J. The lithium chloride was purified with chlorine gas, using the method of Maricle and Hume (*5*). The lithium chloride melting point was 606.8° C. The lithium fluoride was in the

Thermal analysis has been used to determine the temperature-composition solid-liquid phase diagram for the lithium hydride–lithium chloride–lithium fluoride ternary mixture. The diagram of the crystallization surface consists of two areas, a large field comprising a series of solid solutions continuous between LiH and LiF with an undetermined possible LiCl content, and a smaller field of pure lithium chloride. The minimum liquidus temperature in this system, at 459° C., lies at the intersection of these two fields.

form of fine, relatively anhydrous crystals which were dehydrated under vacuum at 150° C. The solid lithium fluoride melting point was 848.0° C. Lithium hydride was prepared by bringing a high purity liquid lithium metal in contact with purified hydrogen at 750° C. (*4*). The lithium hydride melting point was 686.4° C.

Temperatures were measured with a platinum–platinum 10% rhodium thermocouple, which was calibrated against NBS pure Zn (m.p. 419.5° C.) and NBS pure Al (m.p. 660.0° C.). The accuracy of the absolute value of the temperature was estimated to be ±0.3° C.

The pure crystalline salts were weighed into a 347 stainless steel sample crucible in a high purity helium-atmosphere box and introduced directly into a furnace well connected to the floor of the box. Before the sample was heated, the furnace well was sealed from the helium atmosphere of the box, evacuated, and filled with pure hydrogen to about 1-atm. pressure. The sample was then melted and held in the liquid state for 1 hour. The temperature was decreased slowly and the first break in the cooling curve observed. This operation was repeated until the location of the first break was consistent, after which complete cooling and heating curves were determined. This procedure was followed to ensure complete mixing of the components in the system. The final temperature of the solid-liquid equilibrium determined by both heating and cooling agreed to within ±2° C.

DISCUSSION

The LiCl-LiF binary system was investigated by Haendler, Sennet, and Wheeler (*3*), who reported the eutectic composition at 30.5 mole % LiF melting at 501° C. These data have been confirmed by studies carried out in this laboratory, and are used in this report. This binary system was first reported by Botschwar (*2*) and later by Bergmann and Banashek (*1*). Their data are not in agreement; they differ in the liquidus temperature over a wide concentration range and in both the eutectic temperature and eutectic composition. Botschwar reported the eutectic composition at 20 mole % LiF and the eutectic temperature as 485° C. Bergmann and Banashek (*1*) reported the eutectic to be composed of 30.5 mole % LiF. melting at 484° C.

The LiF-LiH system was investigated by Messer and Mellor (*6*), who found continuous series of solid solutions with a very shallow minimum at 684° C. at 15.4 mole % LiF. These data were used without further confirmation.

The LiH-LiCl binary system was investigated by Johnson, Wood, and Crouthamel (*4*). The hydride and chloride of lithium form a eutectic system with a eutectic composition of 34.0 mole % LiH melting at 495.6° C.

The data of Haendler, Sennet, and Wheeler (*3*) for the LiCl-LiF system, of Messer and Mellor (*6*) for the LiF-LiH system, and of Johnson, Wood, and Crouthamel (*4*) for the LiH-LiCl system are given in Figure 1.

Table I. Crystallization Temperatures for the System LiH-LiCl-LiF

Series I, Mole Ratio LiH:LiF 1:9		Series II, Mole Ratio LiH:LiF 3:7		Series III, Mole Ratio LiH:LiF 1:1		Series IV, Mole Ratio LiH:LiF 7:3		Series V, Mole Ratio LiH:LiF 9:1	
LiCl mole fraction	Temp., ° C.	LiCl mole fraction	Temp., ° C.	LiCl mole fraction	Temp., ° C.	LiCl mole fraction	Temp., ° C.	LiCl mole fraction	Temp., ° C.
0.000	832.4	0.000	778.5	0.000	704.4	0.000	692.0	0.000	684.2
0.150	779.0	0.100	754.4	0.100	688.8	0.100	662.0	0.100	656.6
0.301	717.6	0.200	714.4	0.200	662.0	0,200	626.2	0.200	629.6
0.400	663.4	0.400	628.3	0.300	620.3	0.300	595.4	0.300	604.1
0.500	608.0	0.450	598.1	0.400	577.2	0.400	562.9	0.400	576.1
0.550	571.2	0.500	571.0	0.500	518.9	0.500	526.2	0.500	544.5
0.600	544.1	0.550	541.5	0.550	487.7	0.600	483.2	0.550	531.0
0.650	511.6	0.600	498.9	0.600	462.6	0.700	507.0	0.600	515.1
0.750	521.1	0.700	499.9	0.650	483.0	0.800	543.2	0.700	510.0
0.800	532.2	0.750	520.7	0.700	503.9	0.900	576.5	0.800	546.1
0.856	558.7	0.800	538.4	0.750	523.1	1.000	606.8	0:900	581.3
0.950	592.0	0.900	574.0	0.800	539.4			1.000	606.8
1.000	606.8	1.000	606.8	0.900	574.5				
				1.000	606.8				

Series VI, Mole Ratio LiCl:LiF 7:3		Series VII, Mole Ratio LiCl:LiF 3:1		Series VIII, Mole Ratio LiCl:LiF 7.75:2.25		Series IX, Mole Ratio LiCl:LiF 4:1		Series X, Mole Ratio LiCl:LiF 8.5:1.5	
LiH mole fraction	Temp., ° C.	LiH mole fraction	Temp., ° C.	LiH mole fraction	Temp., ° C.	LiH mole fraction	Temp., ° C.	LiH mole fraction	Temp., ° C.
0.000	501.0	0.000	519.5	0.000	528.5	0.000	538.5	0.000	556.0
0.101	494.7	0.100	490.0	0.100	500.3	0.100	511.2	0.100	528.5
0.196	492.2	0.151	470.3	0.150	484.5	0.175	487.0	0.186	503.1
0.225	494.3	0.180	461.3	0.175	476.1	0.200	478.4	0.221	491.3
0.296	516.1	0.190	459.3	0.200	468.8	0.226	468.7	0.250	475.6
0.408	555.6	0.200	460.4	0.210	462.6	0.250	464.6	0.275	475.3
0.496	578.8	0.249	483.5	0.216	460.3	0.275	482.8	0.300	489.5
1.000	686.0	0.299	507.4	0.227	460.5	0.300	493.8	0.400	533.8
		0.335	522.6	0.250	475.9	0.400	536.2	0.500	570.0
		0.400	545.1	0.350	521.8	0.500	570.0	1.000	686.0
		0.500	577.0	0.450	558.2	1.000	686.0		
		1.000	686.0	1.000	686.0				

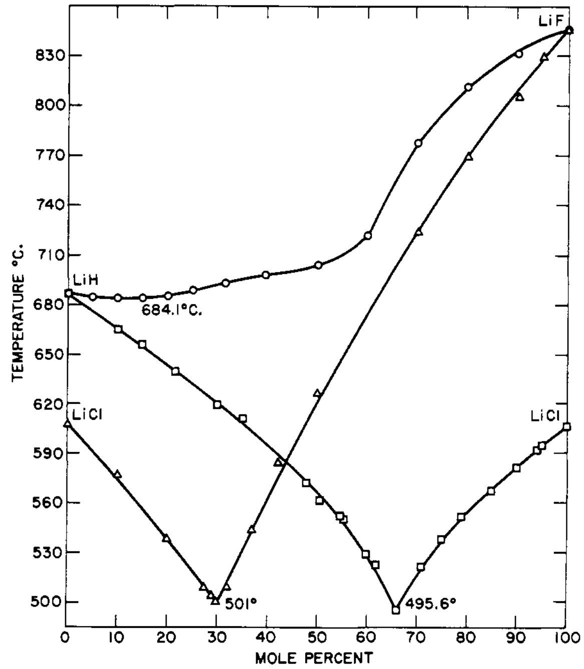

Figure 1. Binary systems LiCl-LiF, LiCl-LiH, and LiH-LiF

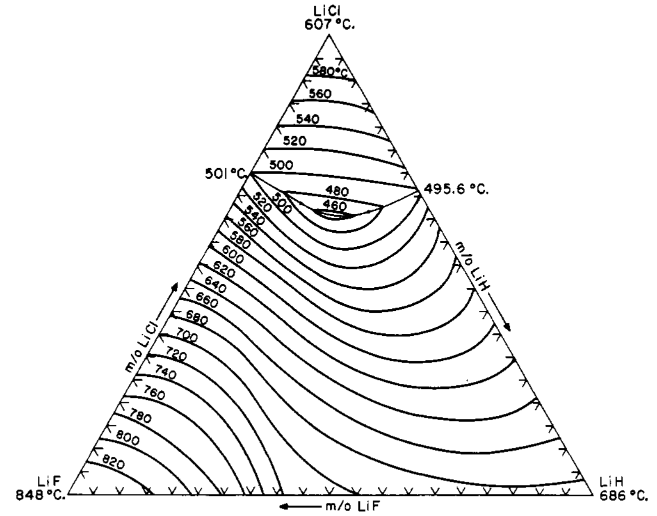

Figure 2. Temperature isotherms for solid-liquid equilibria in the system LiH-LiCl-LiF

The present investigation was mainly concerned with the liquidus surface and not with the complete characterization of the ternary system. Liquidus temperature data for different LiH:LiF mole ratios radiating from the lithium chloride corner of the ternary system are given as series I to V in Table I. In addition, partial cross sections (series VI to X) were studied for LiCl:LiF mole ratios radiating from the LiH corner of the ternary system in order to describe the area of the minimum completely. A contour diagram of the liquidus isotherms for the ternary system, given in Figure 2, was constructed from the quasi-binary systems described in series I to X. Inspection of the liquidus surface of Figure 2 indicates two fields of crystallization: that of pure LiCl and the solid solutions of LiH-LiF. The intersection of these two fields is represented by the curve connecting the eutectic temperatures of the two binary systems, 495.6° C. for LiH-LiCl and 501° C. for LiCl-LiF. This curve has a minimum at 459° C.

A thermal arrest at 440° C. was observed in many of the cooling curves. It was particularly strong for compositions in the solid solution region of the system, and was very weak or almost nonexistent for compositions in the region of solid lithium chloride. In the solid solution region of the diagram this exothermic halt was constant and independent of the length of the terminal halt at the minimum freezing point in the system. A careful investigation of the compositions inside the 460° C. isotherm of Figure 2 showed that only a shallow minimum at 459° C. exists in this surface. Further examinations were made of the LiH-LiF, LiH-LiCl, and LiCl-LiF binary systems for a halt at 440° C., but none was found. This arrest might be caused by a metastable condition in the solid solutions as they are formed or a mechanical effect which alters the established temperature gradients in the apparatus.

ACKNOWLEDGMENT

The authors thank Scott E. Wood for discussions which contributed to the interpretations presented in this paper.

LITERATURE CITED

(1) Bergman, A.G., Banashek, E.I., *Izv. Sektora Fiz. Khim. Anal., Akad. Nauk SSSR* **23**, 201 (1953); *CA* **48** 9170a (1954).
(2) Botschwar, A.A., *Z. Anorg. Chem.* **210**, 163 (1933).
(3) Haendler, H.M., Sennet, P.S., Wheeler, C.M., *J. Electrochem. Soc.* **106**, 264 (1959).
(4) Johnson, C.E., Wood, S.E., Crouthamel, C.E., *Inorg. Chem.* **3**, 1487 (1964).
(5) Maricle, D.L., Hume, D.N., *J. Electrochem. Soc.* **107**, 354 (1960).
(6) Messer, C.E., Mellor, J., *J. Phys. Chem.* **64**, 503 (1960).

RECEIVED for review February 1, 1966. Accepted April 13, 1966. Work performed at Argonne National Laboratory, operated by the University of Chicago under the auspices of the U. S. Atomic Energy Commission, Contract W-31-109-eng-38.