Phase Diagrams of the Systems LiI–KI and LiI–RbI

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The phase diagrams of the systems lithium iodide–potassium iodide and lithium iodide–rubidium iodide have been determined by using the thermal analysis technique together with calculations based on a model proposed by Lumsden. The lithium iodide–potassium iodide system is a simple eutectic, the eutectic occurring at 285° C. and 63.5 mole % LiI. In the lithium iodide–rubidium iodide system, a peritectic occurs at 260° C. and 56.15 mole % LiI, and a eutectic occurs at 252° C. and 62.0 mole % LiI.

WHEN MIXED with lithium iodide, potassium iodide and rubidium iodide form low-melting eutectics. Further, their thermodynamic stability in the presence of molten lithium metal indicates the potential application of these salt mixtures as electrolytes for the lithium-chalcogen cells being developed in this laboratory (*1*, *2*, *10*). The phase diagram for the LiI-KI system has been reported by Leiser and Whittemore (*6*) and by Liu and Lieto (*7*). The lack of agreement between these data has been resolved and new data are given for the LiI-RbI system.

EXPERIMENTAL

The lithium iodide was obtained from two sources. Material from Anderson Physics Laboratories was purified by the Laitinen *et al.* (*5*) method of purging with HI and argon in the molten state, and evacuation to remove the last traces of moisture. The other material was obtained as the trihydrate from Foote Mineral Co. The pure $LiI \cdot 3H_2O$ was dehydrated under vacuum in stages of increasing temperature over a period of two weeks. The LiI thus produced was melted and filtered through a fine quartz frit. The salt was tested for dryness by introducing molten lithium held on a stainless steel sponge. The absence of gas evolution confirmed the dry state of the lithium iodide. Portions of the salt were dissolved in distilled water. The pH of the resulting solution was the same as distilled water, indicating the absence of lithium oxide or lithium hydroxide. Potassium iodide and rubidium iodide were dried by similar programmed vacuum drying of the reagent-grade materials; their dryness and basicity were tested as before by introduction of molten lithium and pH measurement of a water solution of the respective salt.

The solid-liquid equilibrium temperatures in the LiI-KI and LiI-RbI systems were determined by thermal analysis techniques. Cooling rates varied from 1.2° to 2° C. per minute. All the experiments were carried out in furnace wells attached to the floor of a high-purity helium atmosphere box (*4*). Weighed amounts of the respective iodides were placed in the crucible and heated to 500° to 600° C. with stirring until a homogeneous melt was formed. The sensing thermocouple was calibrated against NBS pure tin (m.p. 231.88° C.). In all cases, the thermal arrests at the liquidus and solidus were reproducible to within ±1° C.

RESULTS AND DISCUSSION

The phase diagrams of the two binary systems are given in Figures 1 and 2; the experimental data are presented in Table I. With these minimal data and calculations made using a model proposed by Lumsden (*8*, *9*), the complete binary diagrams were determined. With Lumsden's model, one can calculate the liquidus temperature, T° K., at which pure XZ phase separates in a XZ-YZ mixture:

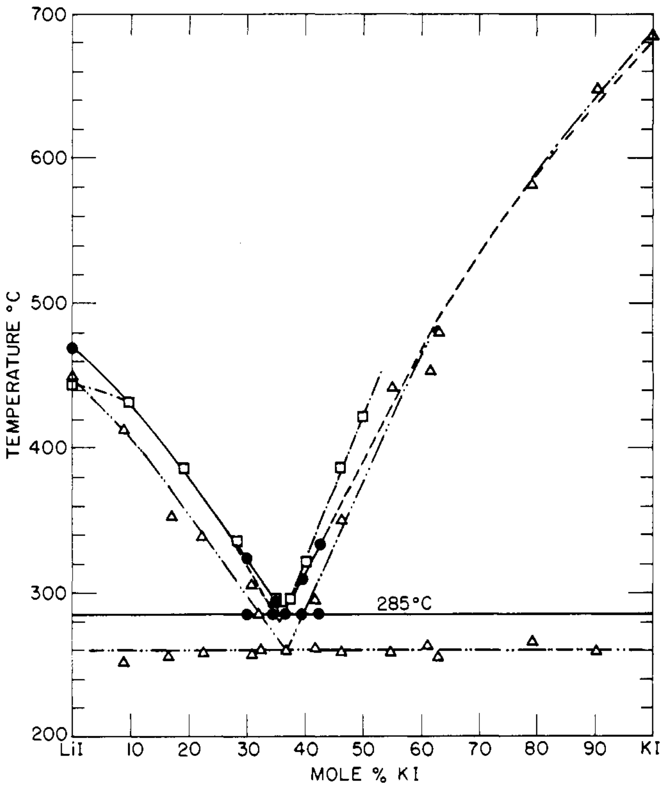

Figure 1. Phase diagram for the system LiI–KI

—●— This study
-------- Calculated
–··—··–△–··—··– Leiser and Whittemore
–·—·–□–·—·– Liu and Lieto

$$T = \frac{KN_y^2 + \Delta H_{f,x}}{(\Delta S_{f,x} - R \ln N_x)} \tag{1}$$

Correspondingly, the liquidus temperature at which pure YZ separates will be given by the relationship

$$T = \frac{KN_x^2 + \Delta H_{f,y}}{(\Delta S_{f,y} - R \ln N_y)} \tag{2}$$

where N_x, $\Delta H_{f,x}$, and $\Delta S_{f,x}$ are the mole fraction of XZ in the mixture, enthalpy, and entropy of fusion of pure XZ, respectively. The subscript y refers to the component YZ in the mixture. K is the interaction parameter which is calculated as the sum of K_L due to the London forces, and K_p due to the polarization forces. The necessary param-

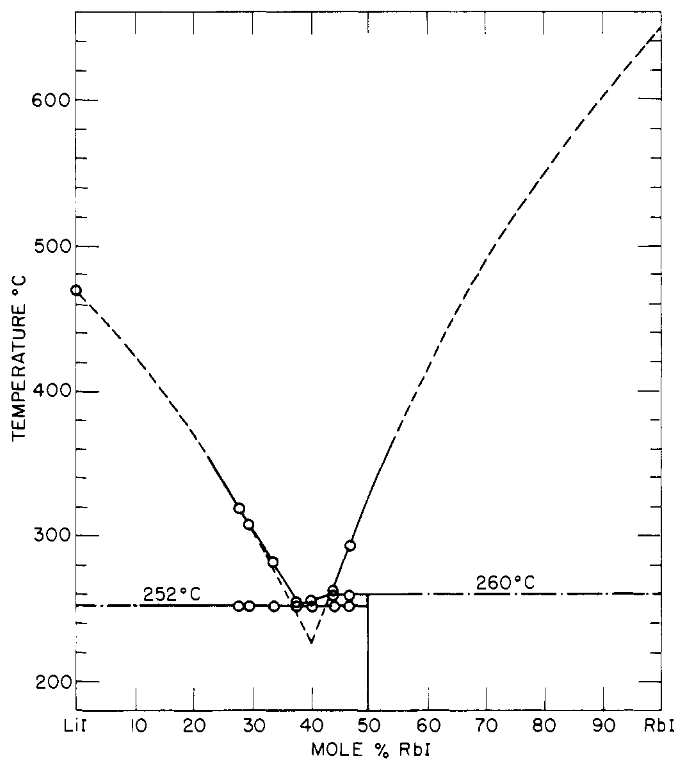

Figure 2. Phase diagram for the system LiI–RbI

- - - - - - - - Calculated

——○—— Experimental

—·—·—·—·— Extrapolated

Table I. Solid-Liquid Equilibria in LiI–KI and LiI–RbI Systems

Mole % LiI	Liquidus Temp., °C.	Eutectic Temp., °C.	Peritectic Temp., °C.
	LiI-KI		
70.0	324	285	...
65.3	295	285	...
63.5	285	285	...
60.5	309	285	...
57.5	332	285	...
	LiI-RbI		
72.0	318	252	...
70.5	308	252	...
66.5	292	252	...
62.5	255	252	...
60.0	257	252	...
56.0	263	252	260
53.5	292	252	260

eters have been summarized by Lumsden (*8*, *9*) and by Dworkin and Bredig (*3*). Equations 1 and 2 are strictly valid only when the solid phase separating is one of the pure components. In the application of Lumsden's method to the data, with no experimental evidence for the presence of solid solutions, it was assumed that only the pure solid component was precipitating from the mixture.

The data of Leiser and Whittemore and those of Liu and Lieto are given in Figure 1 for comparison. From Figure 1, it can be seen that there is good agreement between the present experimental points and the calculated liquidus. There is excellent agreement between the present data and those of Liu and Lieto in the composition range 90 to 60 mole % LiI, including the eutectic composition and temperature. In the composition range 60 mole % LiI to pure KI, the present results extrapolated using the Lumsden-type calculation are regarded as the correct liquidus. The disagreement in the range pure to 90 mole % LiI arises from the discrepancy in the melting point of pure LiI. The authors found a value of 469° C., which is in agreement with the literature (*9*).

The poor agreement between Leiser and Whittemore's data and the present study is considered to be due to the possible presence of H_2O in the LiI used in the Leiser and Whittemore study. These workers melted the $LiI \cdot 3H_2O$ either alone or with KI until gas bubbling stopped in order to obtain LiI or the LiI–KI mixture. As it is very difficult to prepare LiI water-free, the above procedure would result in H_2O dissolution in the melt, with the formation of LiOH. This would lower the melting point of LiI, and the eutectic would probably correspond to a ternary mixture with H_2O in some form. This lowering of the melting point would become smaller with decreasing amounts of LiI in the melt. This appears to be the condition, in that as the mixture becomes richer in KI, there is better agreement with our data.

The thermal analysis data obtained for LiI–RbI indicated the existence of a peritectic in this system. The formation of a 1-to-1 compound has been suggested as the compound decomposing peritectically; however, the existence of this compound has not been experimentally verified. It was estimated that a 1-to-1 compound in the LiI–RbI system might raise the calculated eutectic temperature about 20° C. and have a eutectic composition richer in lithium iodide. The experimental data of Figure 2 confirm this. There is good agreement between the calculated and experimental liquidus, except near the region where the proposed LiI–RbI compound separates as the pure phase. Experimental effort can be minimized, if prior calculations are performed based on the available literature data. In this regard, Lumsden's approach has certain drawbacks. It can be applied easily only to simple eutectic systems with no solid solution or compound formation. The factors Lumsden derived for the calculation and the assumption of regular solution behavior can be challenged. However, for a majority of the alkali halide systems, this model can be applied effectively and seems to be of practical importance.

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