Phase Diagram of the Lithium Iodide–Potassium Iodide System and Densities of the Lithium Iodide–Potassium Iodide and Lithium Bromide–Potassium Bromide Eutectics

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The phase diagram of the lithium iodide–potassium iodide system has been measured by a visual-thermal method. A simple eutectic is formed. The densities of this and the lithium bromide–potassium bromide eutectic melts were determined by the buoyancy method at various temperatures, and the results fitted to equations of the form $\rho = \alpha - \beta t$ by regression analysis.

THE EUTECTIC MELTS of lithium chloride–potassium chloride and lithium bromide–potassium bromide are familiar to molten salt researchers. The chloride melt in particular has been extensively used as the solvent in a variety of studies. The density of this melt at various temperatures has been determined (3). No work on the related iodide system has been reported; one obvious reason for this lack of investigation is the difficulty of obtaining lithium iodide in pure anhydrous form. This paper reports the phase diagram of the lithium iodide–potassium iodide system and the density of the eutectic mixture. The density of the lithium bromide–potassium bromide eutectic has also been measured.

EXPERIMENTAL

Commercial reagent grade chemicals were recrystallized before use. The lithium bromide–potassium bromide eutectic mixture was first dried by evacuation and melted in a quartz apparatus under a hydrogen bromide atmosphere. The hydrogen bromide was removed by repeated flushing with dry argon and evacuation. The eutectic melt was then filtered through a quartz frit. Potassium iodide was prepared in the same manner, except that hydrogen iodide was used in place of hydrogen bromide. As expected, there was considerable decomposition of hydrogen iodide at elevated temperatures. All traces of hydrogen iodide and its decomposition products were removed by repeated purging and evacuation. In the case of lithium iodide, the recrystallized trihydrate was first dehydrated by evacuation while the temperature was gradually raised to approximately 400° C. The product was then sublimed twice under vacuum in a quartz-enclosed tantalum can.

The phase diagram was determined by visual-thermal measurements. The appearance or disappearance of precipitates in the melt was observed through a small observation window in a vertical tube furnace while the temperature of the melt was slowly lowered or raised. The temperature of the liquidus was taken as the average of the results from the increasing and decreasing heat cycles. The maximum deviation of the liquidus temperature from the average between the two cycles was 0.5° C. The eutectic temperature was easily determined by the long temperature stall at the freezing point.

The densities were determined by the buoyancy method. A platinum bob of known weight was immersed in the melts and weighed. The densities of the melts were determined from the observed weight losses. The apparatus and experimental procedures are described elsewhere (2).

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RESULTS AND DISCUSSION

The results of the freezing point measurements on the lithium iodide–potassium iodide system are presented in Table I. The phase diagram of the system is shown in Figure 1. A simple eutectic is formed. The eutectic composi-

Table I. Freezing Point Measurements

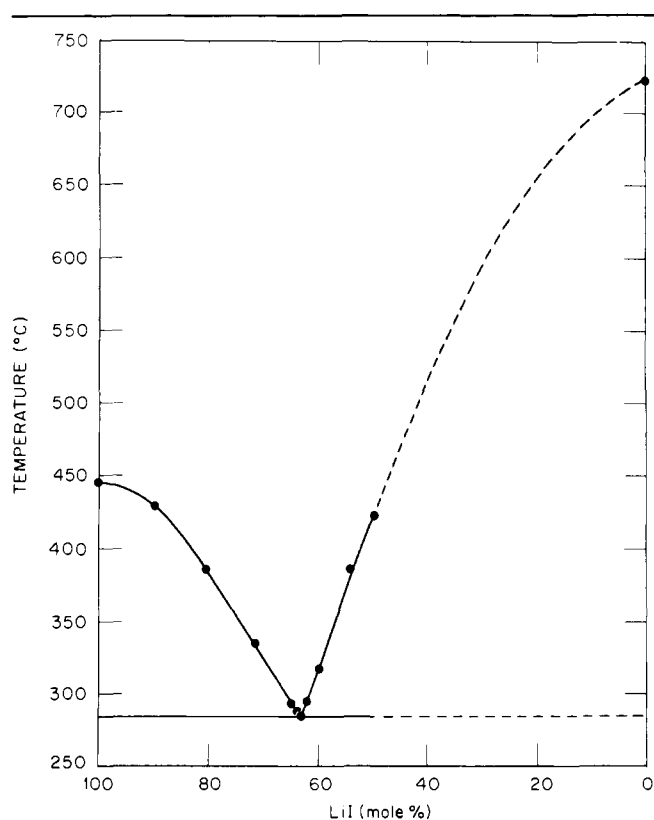| Mole % LiI	Freezing Point, ° C.
89.9	429.2
80.5	385.6
71.4	335.5
64.9	296.2
63.5	287.9
63.2 (eut.)	286.8
62.2	295.3
59.8	321.2
54.0	386.8
49.9	422.4

Figure 1. Phase diagram for system LiI–KI

Table II. Density Measurements

Eutectic Melt	α, G./Cc.	$\beta \times 10^4$, G./Cc./ °C.	Std. Dev. of $\rho \times 10^3$, G./Cc.	Temp., Range, °C.
63.2 mole % LiI-KI	3.350	9.863	1.4	303.6–499.1
60.0 mole % LiBr-KBr	2.860	8.084	2.5	399.1–761.9

tion is 63.2 mole % lithium iodide, and the eutectic temperature is 286.4° C. When the iodide melts are free from moisture, they are stable and can be kept in borosilicate glass or quartz containers. If a trace of moisture is present, hydrogen iodide is evolved, and the alkaline residues attack borosilicate glass and quartz quickly. The composition of the lithium bromide–potassium bromide eutectic is 60.0 mole % lithium bromide (1).

The density data were fitted to the equation $\rho = \alpha - \beta t$ by the method of least squares, where ρ is the density, α and β are constants, and t is the temperature in °C. The results are presented in Table II. Measurements were made at 12 and nine different temperatures for the bromide and iodide melts, respectively.

LITERATURE CITED

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Vapor Pressures and Heats of Sublimation of Cobalt Dihalides

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The vapor pressures of CoF_2, $CoCl_2$, $CoBr_2$, and CoI_2 were measured by the Knudsen-effusion and torsion-effusion techniques. The results were analyzed by computer, and the uncertainties shown are the standard deviation of the least squares fit to the curves. Standard heats of sublimation are those determined using free energy functions calculated from estimated parameters. Derived heats of sublimation were corrected for partial dimerization where mass spectrometric data were available, and second-law and third-law values of sublimation energies were compared.

$\mathbf{A}$CCURATE THERMODYNAMIC constants for many of the metal dihalides are lacking, although Brewer et al. (1) have estimated values for most of them. This study is the first product of a systematic attempt by the Bureau of Mines to characterize these vaporization processes more completely and establish more accurate thermodynamic data. The cobalt dihalides were the first of this series to be investigated by the Knudsen-effusion (7) and torsion-effusion (13) methods simultaneously. There are apparently no experimental data available on CoI_2, and the data on $CoBr_2$ and CoF_2 are limited. Kana'an, Besenbruch, and Margrave (6) studied CoF_2 by the Knudsen and Langmuir techniques, and mass spectrometric studies were made on $CoCl_2$ and $CoBr_2$ by Schoonmaker, Friedman, and Porter (12). Maier (8) and Schaefer (10) studied the vapor pressure of $CoCl_2$ at higher temperatures.

Data reported here were obtained by both Knudsen-effusion and torsion-effusion measurements on purified samples. Commercial cobalt difluoride and cobalt dichloride were purified by vacuum dehydration. Cobalt dibromide was prepared by the reaction of cobalt carbonate powder and hydrobromic acid. The solution was evaporated on a steam bath until purple crystals of cobalt bromide hexahydrate formed. The sample was then treated by vacuum dehydration at 450° C. until an ultimate pressure of 1 × 10^{-5} mm. of Hg was attained. Analyses of the final products are shown in Table I.

Cobalt iodide was prepared by direct combination of the elements in a sealed tube. High purity cobalt metal in the form of machine turnings was placed in a borosilicate glass tube with a slight excess of iodine. The end of the tube containing the reactants was cooled in liquid nitrogen

while the tube was evacuated to less than 10^{-5} mm. of Hg and then sealed. After iodine was sublimed away from the cobalt metal to the opposite end of the tube, the tube was placed in a two-zone furnace and the end containing the iodine was heated to 200° C. to provide approximately 1-atm. pressure of iodine. The end containing the cobalt was heated to 400° C. and the reaction was allowed to proceed. Excess iodine was removed from the CoI_2 by subliming it to the other end of the tube. The tube was broken open in an inert atmosphere glove box and the CoI_2 removed. The average chemical analyses of several samples is shown in Table I.

Table I. Analyses of Cobalt Dihalides

Compound	Metal-Halogen Ratio	
	Chemical analyses[a]	Theoretical
CoF_2	1.506 ± 0.014	1.551
$CoCl_2$	0.838 ± 0.010	0.831
$CoBr_2$	0.367 ± 0.004	0.369
CoI_2	0.232 ± 0.002	0.232

	Spectrographic Impurity Analysis		
	Fe, %	Mn, %	Ni, %
CoF_2	0.003–0.03	0.003–0.03	0.40[b]
$CoCl_2$	0.003–0.03	0.003–0.03	0.44[b]
$CoBr$	0.003–0.03	0.003–0.03	0.01–0.1
CoI_2	0.03 –0.3	0.01 –0.1	0.03–0.3

[a] Uncertainties shown are standard deviations of analyses of six samples. [b] Wet chemical analysis.