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Solid-Liquid Phase Equilibria in Potassium–Cesium Alloy System

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Thermal methods were used to determine in detail the solid-liquid phase equilibria diagram for the potassium–cesium system. The system is a solid solution of continuously varying composition. The minimum in the liquidus curve occurs at 235.12° K and 0.498 ± 0.005 mole fraction cesium. Occurrence of the minimum so near to the 1–1 composition suggests the possibility of a 1–1 intermetallic compound.

Two previous investigations have been made of the freezing points of solutions of potassium and cesium in order to determine the solid-liquid phase diagram for this system (*2, 4*). Both investigators reported complete miscibility in the solid state with a freezing-point minimum at 50 mol %. The measurements were made a number of years ago without the advantage of platinum resistance thermometry, high-purity chemicals, and high-quality inert atmosphere facilities. As a result there is agreement only in the general shape of the diagram, and there are differences as large as 10° between the actual experimental values.

The accuracy possible with the facilities now available in our laboratory is at least an order of magnitude better than that reported by either of the previous studies. As part of our continuing investigation of alkali metal mixtures, it is desirable to obtain a more detailed and accurate phase diagram of this system. Of special interest is the flatness of the solidus line at compositions around the minimum freezing point. Detailed measurements in this region were planned to investigate the possibility of the formation of either a eutectic mixture or an intermetallic solid compound.

EXPERIMENTAL

Chemicals. High-purity grade potassium certified as 99.97% pure was obtained from MSA Research Corp., Evans City, Pa. High-purity (99.9% minimum) cesium was obtained from the Kawecki Chemical Co., New York. Batch analysis of the material by Kawecki Chemical indicated 0.049 mol % Rb, 0.010 mol % K, 0.025 mol % Na with negligible amounts of other impurities. Oxygen analysis was not performed. However, calculations from the change in melting point of the Cs with fraction melted indicated less than 0.01 mol % oxygen. The cesium is considered to be better than 99.90% pure.

Sample Preparation. The alloy mixtures were prepared and manipulated in a Vacuum Atmospheres Corp. argon glove box. Circulation of the argon through a purification train kept oxygen and water vapor concentrations at <1 ppm. Under these conditions, the liquid alloys showed no oxide formation after several hours in the box and showed only a slight oxide layer when left for several days.

Samples were prepared by weighing the potassium and cesium inside the glove box on a top-loading Mettler P-160 single-pan balance (±0.001 gram accuracy). The samples were weighed into a nickel crucible, melted to form a homogeneous mixture, and then transferred into the freezing-point apparatus. To conserve cesium metal, some samples were prepared in a similar manner by dilution of an alloy sample of known composition with either potassium or cesium.

Apparatus. The apparatus used for making the freezing-point measurements has been described in the literature (*1, 3*). Briefly, it consists of a double-jacketed stainless steel sample tube. Coolant (usually liquid nitrogen) circulating through the outer jacket and a heating tape wound around the outer jacket provide the temperature variability needed to obtain time-temperature cooling and warming curves. The inner jacket is connected to a vacuum/helium exchange gas system. The rate of cooling or warming is controlled by varying the pressure of the He exchange gas in this space as well as by varying the type of circulating coolant or the heater current. Rotary stirring is accomplished by driving a stainless steel stirrer tube with a variable speed motor through a worm gear. The apparatus is suspended inside the argon glove box so that all operations from preparation of sample to freezing-point measurements are made with minimal chance of contamination of the metals with oxide.

Temperature Scale. Temperatures were measured with a Leeds and Northrup platinum resistance thermometer in combination with a Leeds and Northrup high-precision resistance recorder. The thermometer passes down through the center of the stirrer tube in the freezing-point apparatus and into a thermometer well in the center of the sample tube.

The thermometer was calibrated by Leeds and Northrup at the ice, steam, sulfur, and oxygen points. The calibration was checked by us at the ice point (273.150° K), the mercury freezing point (234.29° K), and the sodium sulfate decahydrate transition temperature (305.534° K) before, during, and at the conclusion of the measurements. In all cases

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the value obtained agreed with the calibration to within ±0.01° K. We estimate our temperature scale to be accurate to at least ±0.02° K over the range of the experimental measurements.

RESULTS

Solidus and liquidus points were determined over the entire composition range from thermal measurements. At least three successive time-temperature cooling and warming curves were obtained for each sample. The solidus and liquidus temperatures were obtained in each of the runs from both the cooling and warming curves. The agreement was well within the experimental error as given below, indicating that phase segregation was not a problem in the determination of the solidus point. The results of the measurements are summarized in Table I and the phase diagram is shown in Figure 1. The liquidus points are considered accurate to ±0.15° K. The uncertainty in the solidus points varied in different regions of the phase diagram. Figure 2 gives representative time-temperature cooling and warming curves at various compositions. As can be seen from this figure, in the region around the freezing-point minimum (0.45-0.55 mole fraction Cs) the time-temperature curves are very flat. It was easy to detect the solidus point in this region directly from the time-temperature curves to within ±0.2° K. Over the rest of the diagram, the slope of the time-temperature curves was too steep to determine the solidus point directly. When this occurred, uncertainty in the extrapolation to the solidus point was decreased by replotting the data in a form dictated by an equation derived from Newton's law of cooling. In effect, the temperature function used is a linear function of time for that part of the warming process prior to the start of melting. When the data are plotted in this form, the point at which deviation from a straight line graph occurs gives the solidus point. The sensitivity of the method is increased by plotting a difference function, a line obtained from a linear least-squares fit of the straight-line portion of the graph being subtracted from the temperature function before plotting. The details of this method are given in an earlier paper (*3*). Figure 3 shows representative plots of the curve straightening technique at the compositions of 0.1999 and 0.7970 mole fraction cesium. Comparison of Figure 3 with the warming curves at this same mole fraction in Figure 2 illustrates how well the curve-straightening technique emphasizes the solidus break. Using this technique, we estimate the uncertainty of the solidus points as given in the table to be ±1° K except in the region around the freezing-point minimum (0.45-0.55 mole fraction Cs) where, as previously mentioned, the uncertainty is ±0.2° K. At several compositions, we did not list a solidus point. The curves were too steep to read directly with any precision and the liquidus point is so close to the solidus point that it interfered with the curve-straightening technique.

Table I. Solidus and Liquidus Points in Potassium-Cesium System

Mole fraction cesium	Liquidus point, ° K	Solidus point, ° K	Mole fraction cesium	Liquidus point, ° K	Solidus point, ° K
0.0000	336.86	. . .	0.4917	235.13	234.91
0.0993	312.80	285.9	0.4951	235.12	234.87
0.1999	289.22	258.3	0.5002	235.12	234.89
0.2727	271.62	243.3	0.5102	235.33	234.81
0.2999	265.72	239.8	0.5202	235.68	234.90
0.3756	249.01	235.6	0.5501	237.44	. . .
0.4128	241.73	234.9	0.6103	243.10	237.3
0.4496	236.82	. . .	0.6999	254.62	243.0
0.4732	235.46	234.84	0.7970	268.84	254.0
0.4802	235.27	234.90	0.8997	285.03	274.6
0.4859	235.18	234.88	1.0000	301.59	. . .

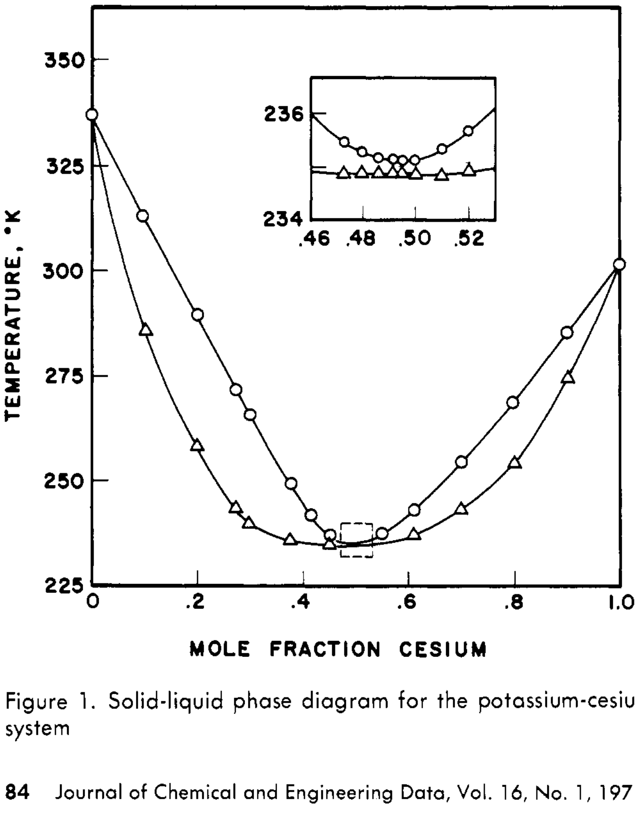

Figure 1. Solid-liquid phase diagram for the potassium-cesium system

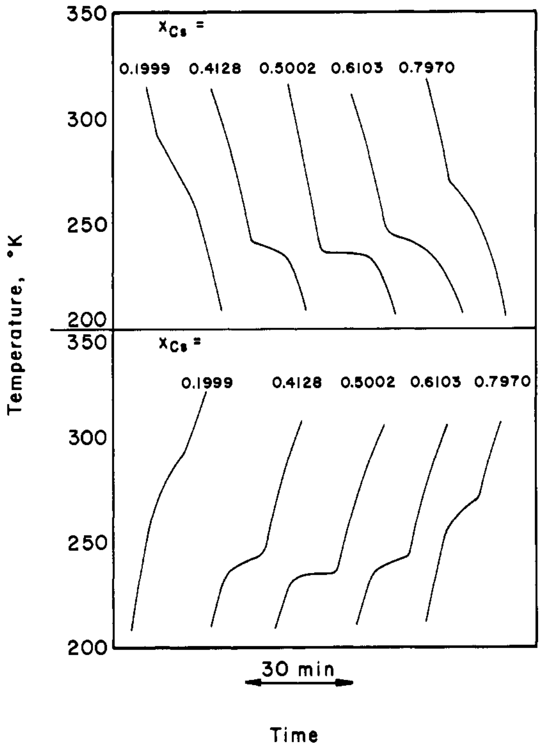

Figure 2. Representative time-temperature cooling (upper) and warming (lower) curves for potassium-cesium mixtures

Potassium and cesium are completely miscible in the solid state with a freezing point minimum occurring at 0.498 ± 0.005 mole fraction Cs (Figure 1). The liquidus line has a zero slope at the freezing-point minimum, which is indicative of solid-solution behavior rather than eutectic formation. Furthermore, while the solidus line gets quite flat, it does have a measurable nonzero slope on either side of the solid solution minimum. The solidus and liquidus

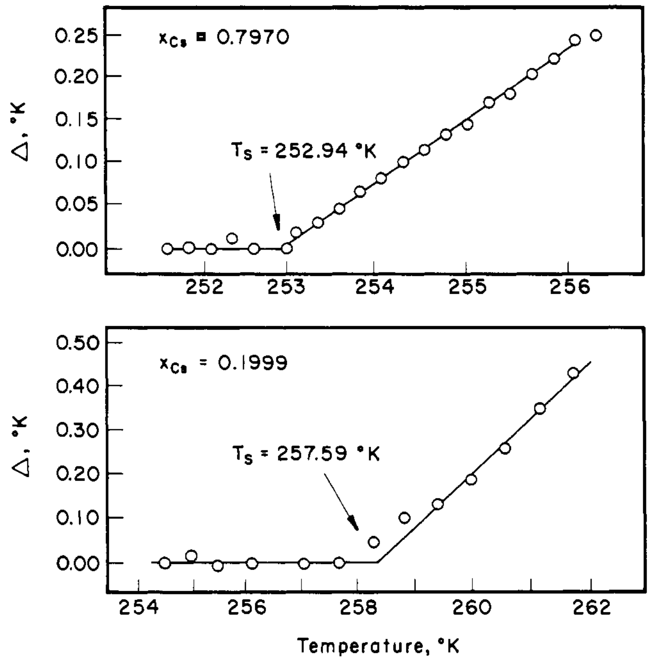

Figure 3. Representative plots of the curve-straightening technique that was used to locate solidus points

curves lack 0.15° K of merging at the freezing point minimum. This is about the difference that would be expected from the 0.1 mol % impurity in the samples.

The occurrence of the minimum (within experimental error) at a 1–1 stoichiometric composition suggests the possible formation of a 1–1 intermetallic compound. The thermal data alone, however, are not sufficient to confirm the existence of a compound.

Our results are in much better agreement with the earlier work of Rinck (*2*) than with that of Goria (*1*). Although Rinck's data show considerable scatter, the smoothed curve through his experimental points agrees with our results to within ±1° K. Agreement with the data of Goria (*1*) is much poorer, the differences being as large as ±8° K.

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Density and Viscosity of Deuterium Oxide Solutions from 5–70° C

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The density and viscosity of deuterium oxide solutions have been measured from 5–70° C. The density measurements were made by a magnetic float technique, and the viscosity measurements were made using a modified Cannon-Ubbelohde viscometer with a semiautomatic optical viscometer reader. The results are briefly discussed and compared to the results obtained by other scientists.

In recent years various workers (*13, 14, 16, 18*) have studied the differences between the thermodynamic and transport properties of deuterium oxide, D_2O, and normal water, H_2O. Many studies (*1, 5*) have also been made on the differences between electrolyte and nonelectrolyte solutions of D_2O and H_2O. The results of most studies (*1, 13, 16, 18*) indicate that D_2O solutions are more structured than H_2O solutions at the same temperature.

This study of the density and viscosity of D_2O solutions was made to provide precise thermodynamic and transport data that may prove useful in elucidating the causes of the structural differences between D_2O and H_2O as a function of temperature.

EXPERIMENTAL

The two samples of D_2O used in this study were obtained from Bio-Rad Chemical Co. and were used without further purification. Although both samples were supplied as 99.88 mole % D_2O, the density determinations indicated that sample No. 1 (used in previous studies, *12*) was 98.35 ± 0.01 mole % D_2O. The decrease in D_2O in sample No. 1 was apparently caused by the exchange with atmospheric water before use. Ion-exchanged (~8 MΩ) H_2O was used in all the calibration runs.

The magnetic float densitometer used to make the density measurements has been described in detail elsewhere (*11*). The densitometer was calibrated using the densities for H_2O tabulated by Kell (*8*). The H_2O and D_2O solutions were degassed before use to prevent the formation of bubbles on the magnetic float during an experiment. The precision obtained in duplicate runs was ±2 ppm. The mole % of the D_2O used in this study was checked from our density measurements using the linear equation, $d_{D_2O} = d_{H_2O} + AX_{D_2O}$ (where d is the density, A is a constant, and X is the mole % D_2O). The constant, $A = (d_{D_2O} - d_{H_2O})/100$, was determined from the density data for 100% D_2O and normal H_2O using the density data tabulated by Kell (*8*). This linear interpolation yielded 98.35 ± 0.01 mole % for sample No. 1 and 99.88 ± 0.01 mole % for sample No. 2 over the entire temperature range. Although the purity of the D_2O determined by this method is dependent

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