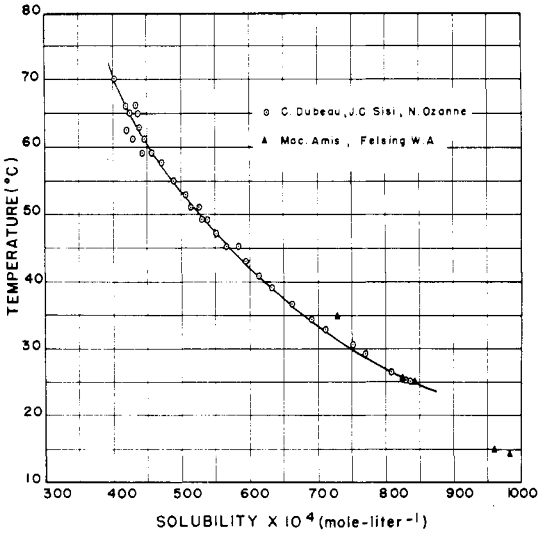

Figure 2. Variation of hydrogen selenide solubility with temperature

equilibrium. The equilibrium is verified by leaving the system standing for 30 min and observing that the pressure remains constant.

RESULTS

The experimental results are reported in Table I. In Table II some values obtained at higher temperatures are reported. These values are highly affected by experimental errors. They are therefore ignored in the solubility calculation.

The experimental values given in Table I were used to calculate the values of the constants appearing in the following equations using a least squares method:

$$S = A + BT + CT^2 \qquad (1)$$

$$\ln S = A' + B'/T \qquad (2)$$

where S is the solubility (moles-liter^{-1}) and T is the temperature (° K). The equations obtained are:

$$S = 1.7583 - 9.664 \times 10^{-3}\, T + 1.3572 \times 10^{-5}\, T^2 \qquad (3)$$

$$\ln S = -8.4278 + 1772.35/T \qquad (4)$$

The normalized errors for the equations are, respectively, 0.000717 and 0.000698.

Thermodynamically, the slope of the linear Equation 4 represents the enthalpy of solution divided by gas constant R (*2*). When the experimental values are represented by the linear Equation 4, the value of the enthalpy of solution is

$$\Delta H = -1.772.35 \times R = -3.522 \text{ kcal-mole}^{-1}$$

Since the solution is diluted, Henry's law can be applied,

$$K_h = P/X_2 \qquad (5)$$

where P is the partial pressure of hydrogen selenide expressed in atmospheres and X_2, the hydrogen selenide molar fraction in the solution.

Since the number of moles of hydrogen selenide in the solution is negligible when compared with the number of moles of solvent, the values of the constant K_h as function of the temperature can be obtained from the equation,

$$\ln K_h = 12.4425 - 1772.35/T \qquad (6)$$

DISCUSSION

The solubility values obtained are precise to within 1% for temperatures lower than 50° C. At higher temperatures, because of the larger experimental errors especially between 60° and 70° C, the precision is lowered.

On the other hand, the calculated enthalpy value of −3.522 kcal-mole^{-1} falls between the only two old values reported in the literature, namely −4.630 kcal-mole^{-1} obtained by Fabre (*1*) and −2.431 kcal-mole^{-1} obtained by McAmis and Felsing (*3*).

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RECEIVED for review June 2, 1970. Accepted October 12, 1970.

Thermal Conductivity of Phosphoric Acid–Water Mixtures at 25° C

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A thermal conductivity cell of the transient hot-wire type, used in conjunction with an improved potentiometric measurement method, is described and shown to give reliable results for aqueous ortho-phosphoric acid–water mixtures at 25° C.

Measurements of the thermal conductivities of liquid ortho-phosphoric acid (H_3PO_4) and an 87% aqueous solution in the temperature range 20–130° C have been previously reported by this author (*18*). A transient hot-wire probe, consisting of an electrically heated bare platinum wire immersed in the liquid, was used. More recently, Luff and Wakefield (*13*) reported the thermal conductivities of aqueous phosphoric acid solutions in the concentration range 84–115% H_3PO_4 (60–83% P_2O_5) and the temperature range 25–150° C. They used a modified transient probe, consisting of an electrically heated manganin wire and copper-constantan thermocouple in a glass capillary. In the area of overlap, 87–100% H_3PO_4 and 25–130° C, the results of Luff and Wakefield (*13*) are 5–7% lower than those of this author (*18*). This difference, although barely exceeding the combined limits of error, suggests a small systematic error in one or both sets of results.

To investigate this discrepancy, another series of experiments was performed, using a new hot-wire probe. An improved potentiometric method, employing a digital voltmeter with extremely rapid response, was used for following the wire temperature. The thermal conductivities of seven compositions in the range 0–100% H_3PO_4 at 25° C were measured.

Unsuccessful attempts were made by Luff and Wakefield (*13*) to use the bare-wire probe in phosphoric acid solutions; the lack of success was attributed to polarization of the electrolyte. This problem was not encountered with either my earlier or present probes since the potential drop across the wire was kept low enough to avoid current flow through the liquid. To confirm this, experiments were undertaken to detect any difference between the effective probe resistance in water and in various H_3PO_4 solutions. Due allowance was made for the slightly different temperature rises of the wire in the various liquids. If there was no detectable difference, there would be negligible current flow in the H_3PO_4 solutions, since water is known to be a good insulator. In this case, there would be no interference with the heat flow pattern or the use of the wire as a resistance thermometer.

Table I. Thermal Conductivity of Phosphoric Acid–Water Mixtures at 25° C

Concn, % H_3PO_4	Density, gram cm^{-3}	I_2A	R_i ohms	10^6 $\Delta E/\Delta \ln t$, V	10^4 K cal cm^{-1} sec^{-1} $° C^{-1}$
0		0.19729		166.5	14.73
		0.19707	1.5454	170.0	14.38
		0.19725		167.5	14.63
		0.19725		167.5	14.63
		0.19735		165.0	14.87
					14.65 ± 0.22
20.2	1.1144	0.19742	1.5456	183.0	13.43
		0.19743		183.0	13.43
		0.19738		184.0	13.35
		0.19739		184.0	13.35
		0.19735		185.0	13.27
					13.37 ± 0.09
35.5	1.2190	0.19699	1.5458	196.0	12.46
		0.19735		197.0	12.47
		0.19740		200.0	12.28
		0.19747		197.5	12.46
		0.19747		200.0	12.29
					12.39 ± 0.12
50.5	1.3374	0.19726	1.5461	209.0	11.73
		0.19712		206.0	11.88
		0.19717		209.0	11.72
		0.19721		215.0	11.40
		0.19717		216.0	11.35
					11.62 ± 0.25
71.2	1.5334	0.19739	1.5462	227.0	10.82
		0.19731		229.0	10.72
		0.19731		230.0	10.67
		0.19718		224.0	10.93
					10.79 ± 0.16
87.5	1.7146	0.19850	1.5463	237.0	10.55
		0.19860		243.0	10.30
		0.19865		240.0	10.44
		0.19710		233.5	10.48
		0.19687		232.0	10.51
					10.46 ± 0.12
100.0	1.8710	0.16997	1.5463	231.5	10.55
		0.19717		234.0	10.47
		0.19721		240.0	10.21
		0.19714		237.5	10.31
		0.19711		237.5	10.30
					10.37 ± 0.17

EXPERIMENTAL

Materials. The phosphoric acid solutions were made from high-purity analytical reagent grade 94% H_3PO_4 by dilution at room temperature, or from solution of reagent grade P_4O_{10} at 80–100° C with slow cooling. All solutions were allowed 10 days for equilibration of phosphate species before use. The solution densities at 25.00° ± 0.01° C were measured with a precision of 0.0001 gram cm^{-3} using a 100 cm^3 volumetric flask calibrated with water. The consistency of published density *vs.* composition data (*2, 3, 14*) allowed the solution compositions to be determined with 0.1–0.2% accuracy (Table I). These compositions were confirmed within ±0.5% by analysis for phosphorus using a gravimetric modification of the phosphomolybdate method (*11*).

Probe. A 9.05-cm length of 0.0099-cm-diam platinum wire was welded at each end to leads of 0.05-cm-diam platinum wire. Potential taps of 0.0025-cm-diam platinum wire were lightly welded near the ends of the main wire. The length between taps, 8.35 ± 0.005 cm, was measured with a traveling microscope, which also served to check wire linearity and freedom from weld distortions. The taps were welded to leads of 0.05-cm-diam platinum wire at a radial distance of 1.5 cm from the main wire. All leads were sealed into glass tubes so that only 0.5 cm of lead was exposed, and the tubes were cemented into the stopper of a glass tube of 3.0 cm internal diameter and 20.0 cm length. This tube was deeply immersed in a Dewar vessel held in a water bath controlled at 25.00 ± 0.01° C in a constant-temperature room. The temperature was measured with a precision mercury-in-glass thermometer which was checked against a Dymec 2801A quartz thermometer. The high thermal inertia of the thermostat system prevented short-term temperature fluctuations.

Circuit. Current was supplied by a large-capacity 12-V accumulator to a five-decade resistance box, a standard 1-ohm resistor and a change-over switch which led to either the hot-wire or a matched manganin dummy resistor. Most of the potential across the wire taps was balanced by a Tinsley microvolt potentiometer. The excess potential was measured by a Hewlett-Packard 2212A voltage-to-frequency converter which produced an output of 10^5 Hz for 0.01-V input. This frequency was fed to a Hewlett-Packard 5216 seven-digit counter operated with 0.1-sec gate time to give a digital reading of potential with 1-μV sensitivity. Checks against the potentiometer showed the digital meter to have an accuracy of ±1 μV for readings up to 1000 μV. The voltage-to-frequency converter had a slewing rate of 10^6 V sec^{-1} and settling time of 10^{-4} sec to within 0.01% of final pulse rate. Since the maximum rate of change of wire potential under observation was 10^{-3} V sec^{-1}, there was negligible lag in voltage readings.

The digital meter gave a voltage integrated over the 0.1 sec gate time, whereas instantaneous values were required. However, an "equivalent" time, t_e, was defined at which the integrated voltage equaled the instantaneous value. Assuming that $E \propto \ln t$, a mathematical analysis gave the general result

$$\ln t_e = (1/t_c)[(t_i + t_c) \ln (t_i + t_c) - t_i \ln t_i] - 1 \qquad (1)$$

where t_i is the time after commencement at which a count is initiated and t_c is the count time. In the present work t_e was negligibly different from $(t_i + t_c)/2$ for $t_i > 2$ sec.

Operation. After an initial 2-hr settling period, the drift in potential drop across the dummy resistor became < 1 μV over a 30-sec period. Current was then switched to the wire, simultaneously initiating the first 0.1-sec count time of the digital meter. Thereafter, successive count times of 0.1 sec were initiated by the internal reset multivibrator of the counter at intervals of about 2 sec. The exact time between resets was found by timing 20 resets with a stopwatch, twice before and twice after each experiment. The constancy of the time interval was within the precision of measurement, ±0.005 sec. After 30 sec, the digital meter was switched to measure the potential across the 1-ohm standard, from which the wire current was obtained. The current was switched back to the dummy at 40 sec, and a period of 30 min was allowed for thermal equilibration. The effective wire resistance at any time during the experiment was obtained from the total wire potential and the potential across the 1-ohm standard.

RESULTS

Thermal Conductivity. The thermal conductivity, K, was calculated from the well-known (*5, 7, 9, 17*) equation

$$K = (q/4\pi)(\Delta \ln t/\Delta R)(dR/dT) \qquad (2)$$

where q is the rate of heat production per unit length of wire, t is the time after commencement of heating, R is the wire resistance between potential taps, and T is the wire temperature. The increase in wire resistance, ΔR, over a given time interval was obtained from the measured increase in potential, ΔE, across the wire. Since the source potential and series resistance were constant, there was a slight fall in current ΔI, over the time interval due to the increase in wire resistance. Previous workers (*9, 20*) measured ΔE and ΔI separately in order to derive ΔR. However, analysis of the circuit (*15*) led to the relation

$$\Delta R = (\Delta E/I_2)[(R_s + aR_1)/R_s] \qquad (3)$$

where R_s is the fixed series resistance, R_1 is the wire resistance at the start of the time interval, I_2 is the current at the end of the time interval, and a is the ratio of total wire resistance to wire resistance between taps. For the runs reported here, R_s = 61 ohms; $R_1 = 1.546 \pm 0.001$ ohms, and a = 1.085 so that the correction factor in square brackets was 1.027 for all runs.

The start of the time interval in which ΔE measurements could be made was 2 sec after commencement of heating, since, before this, Equation 2 was not applicable (*5, 17*). The end of the time interval was caused by the onset of convectional heat transfer in the liquid and increased from 18 to >30 sec as the H_3PO_4 concentration increased from 0 to 100%. The observed ΔE values were corrected for the effect of differing heat capacities/unit volume of the wire and the liquid. Using previously derived theory (*9*), reported heat capacity data for phosphoric acid solutions (*4*) and platinum (*12*), barely significant corrections were made to each ΔE value, ranging from 1 μV at 2 sec to 0.1 μV at 20 sec. Plots of corrected ΔE *vs.* ln t were linear within the measurement accuracy of ±1 μV within the above-mentioned time intervals. The slopes $\Delta E/\Delta \ln t$, measured with 0.2% precision, are given in Table I.

The temperature coefficient of resistance (dR/dT) was obtained by resistance measurements with the probe in water, using a current of 0.02 amp which caused negligible heating. Twelve measurements in the range 20–40° C taken in random order throughout the work showed excellent reproducibility. A quadratic resistance *vs.* temperature relationship obtained by the method of least squares fitted the data with a mean deviation of 0.0001 ohm, giving R_0 = 1.5433 ohms and $(dR/dT) = (4.046 \pm 0.020) \times 10^{-3}$ ohms °C^{-1} at 25° C. The heating rate q was calculated from

$$q = (I_2^2 R_1)/l \qquad (4)$$

where l is the length of wire between taps. Since the total changes in I and R from commencement were –0.02% and +0.2%, respectively, q was calculated to sufficient accuracy using I_2 and R_1, which were both measured with an accuracy of 0.01% (Table I).

The errors to be expected from other sources such as radial and axial temperature gradients in the wire, nonuniformity of the wire, heat transfer by radiation and the finite outer limit of the liquid have been considered (*9, 17*) and found to be negligible. The temperature rise of the wire at the middle of the experimental time interval ranged from 0.55° for water to 0.85° for phosphoric acid. There was thus negligible error in ascribing all K values to 25° C. Individual values of K, together with means for each concentration and their 95% confidence limits, are given in Table I.

Probe Resistance. To compare the effective resistances of the probe in various liquids, it was necessary to correct for the effect of temperature rise. At any time, t, after commencement of heating, the resistance, R_t, was given by

$$R_t = R_0 + (dR/dT)\,\Delta T \qquad (5)$$

where R_0 is the resistance at zero time at 25° C. The temperature rise ΔT above 25° C depended on liquid properties, current, and time according to the relation

$$\Delta T = (I^2 R/4\pi K l)(\ln 4at/r^2 - 0.5772) \qquad (6)$$

where a is the thermal diffusivity of the liquid and r is the wire radius. This equation is a good approximation to the exact theory for $t > 2$ sec (*5, 17*). Thus, using the known probe dimensions and liquid properties (*2, 4, 19*), it was possible to compare R_0 values for various liquids under the operating conditions used for thermal conductivity measurements. The typical results in Table II for t = 20 sec show identical R_0 values within the expected measurement error of ±0.0002 ohm for water, 50.5% H_3PO_4, and 87.5% H_3PO_4 up to overall potential drops across the wire of 0.6 V. Similar results were obtained for other compositions and times of 2–20 sec.

DISCUSSION

Thermal Conductivity. For comparison with the present results (Figure 1), the data of previous workers were corrected to 25° C using (dK/dT) varying linearly with composition between 3.7×10^{-6} cal cm^{-1} sec^{-1} °C^{-2} for water (*1*) and 2.0×10^{-6} cal cm^{-1} sec^{-1} °C^{-2} for phosphoric acid (*18*). The present result for water at 25° C, 14.65

Table II. Hot-Wire Resistance in Various Liquids at 25° C after Heating for 20 Sec

Liquid	I, A	E, V	R_t, ohms	R_0, ohms
Water	0.09892	0.15273	1.5440	1.5433
	0.15751	0.24337	1.5451	1.5432
	0.21814	0.33748	1.5471	1.5434
	0.28635	0.44375	1.5497	1.5434
	0.34463	0.53501	1.5524	1.5433
50.5 % H_3PO_4	0.09932	0.15337	1.5441	1.5432
	0.15909	0.24593	1.5458	1.5434
	0.22085	0.34190	1.5479	1.5433
	0.29225	0.45333	1.5512	1.5431
	0.34272	0.53259	1.5543	1.5431
87.5% H_3PO_4	0.09916	0.15314	1.5443	1.5443
	0.15724	0.24308	1.5459	1.5433
	0.21880	0.33880	1.5484	1.5434
	0.28876	0.44823	1.5522	1.5434
	0.33874	0.52693	1.5556	1.5435

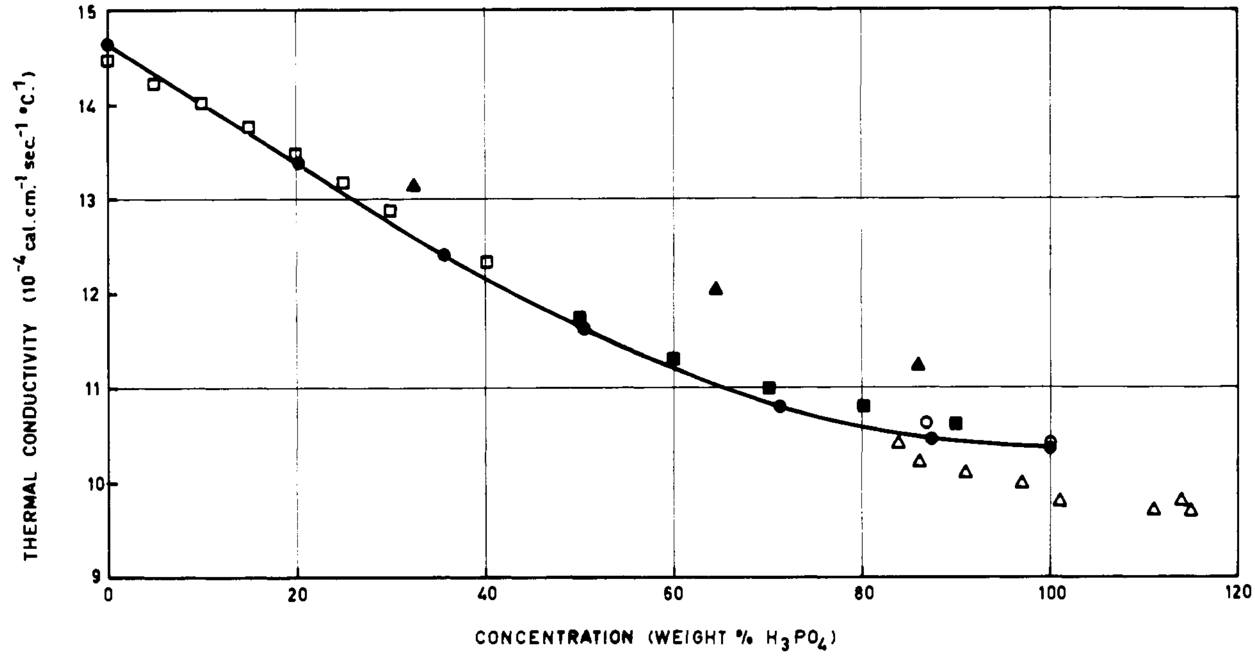

Figure 1. Thermal conductivity of phosphoric acid–water mixtures at 25° C vs. composition

□ Riedel (*16*) corrected from 20° C
■ Riedel (*16*) corrected from 29° C
▲ van der Held, van Drunen (*7*) corrected from 19.5° C
△ Luff, Wakefield (*13*)
○ Turnbull (*18*) corrected from 23° C
● Turnbull, present work

× 10^{-4} cal cm^{-1} sec^{-1} °C^{-1}, is in satisfactory agreement with the results of other recent workers using both transient and steady-state techniques (*1, 6*). For phosphoric acid solutions, Riedel (*16*) reported two sets of data, 0–50% H_3PO_4 at 20° C and 50–90% H_3PO_4 at 29° C, both obtained with a steady-state concentric cylinder method. The first set agree within ±1.5% with the present data, although the slight inflection at about 30% is not found in the present work. The second set also agrees within combined error limits, but falls consistently 1–2% higher.

Near the concentration of commercial acid, 87%, the present value lies only 1.8% below the previous value obtained with a different hot-wire probe and sample (*18*), and only 1–3% above the Luff and Wakefield (*13*) values obtained with a modified hot-wire probe. Luff and Wakefield calibrated their probe using literature data for water, glycerol solutions, and sulfuric acid solutions at 25–100° C. Recalculation of their results, based on only their 25° C calibrations, gives excellent agreement with present work.

For 100% H_3PO_4, the present value agrees with that obtained previously (*18*), but is about 5% above that of Luff and Wakefield (*13*). This may be partly due to lack of equilibration of phosphate species since it is reported (*10, 19*) that there is a slow rate of approach at 25° C to an equilibrium mixture of 88 mol % H_3PO_4, 6 mol % $H_4P_2O_7$, and 6 mol % H_2O. However, there is no evidence of lack of equilibration, since there appeared to be no difference in thermal conductivity between the previous sample, made by boiling of 85% acid, and the present sample, made by solution of P_4O_{10} in 94% acid. Similarly, Luff and Wakefield (*13*) found no difference between preparations made by diluting 114% acid and dissolving P_4O_{10} in 85% acid. Finally, the results of van der Held and van Drunen (*7*) appear to be a little high, possibly due to an incorrect analysis of their thick transient probe as suggested in a subsequent paper (*8*).

Transient Method. The transient hot-wire probe of the present type has been used to obtain the thermal conductivity of water to an accuracy equal to that of the best steady-state methods (*1, 5*). Moreover, it is ideally suited to viscous liquids like phosphoric acid where the period before convection is extended, allowing the use of more temperature-time data points. The probe resistance was identical in water and phosphoric acid solutions having ac conductivities up to a maximum of 0.20 (ohm-cm)$^{-1}$ (*19*) in the observation period of 2–20 sec after potential is applied. Moreover, when observed on a cathode ray oscilloscope, the wire potential drop showed no abnormal behavior, and the potential across the standard ohm showed constancy of current from times as short as 10^{-3} sec. It is suggested that polarization occurred very rapidly in these solutions and prevented current flow through the liquid in parallel with the wire for potential drops less than 1 V. The fact that ΔE *vs.* $\Delta \ln t$ plots were linear in agreement with theory, and that they gave thermal conductivities in agreement with results of steady-state methods may be taken as confirmation that no abnormal current flow occurred in the present application of the transient hot-wire method.

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RECEIVED for review June 8, 1970. Accepted October 2, 1970.

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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