[Contribution from the Oak Ridge National Laboratory, Chemistry Division]

Miscibility of Liquid Metals with Salts. II. The Potassium–Potassium Fluoride and Cesium–Cesium Halide Systems[1]

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Miscibility in all proportions of cesium metal with cesium halides at and above the melting points of the pure salts, and of potassium metal with potassium fluoride fifty degrees above the melting point of the salt was found. Vapor pressure measurements on some of these mixtures confirmed their true solution nature. The temperature–concentration range of coexistence of two liquid phases decreases in going from sodium to potassium systems and disappears altogether for the cesium systems. The solubility of the solid halides in the corresponding liquid alkali metals, at a given temperature, increases greatly with increase of atomic number of the metal. This may be explained by the decrease of cohesive forces in both the metal and its salts as the atomic number of the metal is increased. Partial heats of solution of the solid salts, at saturation, in the liquid metals, also correlate well with the cohesive energies, or heats of vaporization and sublimation, ΔH_v and ΔH_s, of the liquid metals and the solid salts, respectively: CsF, with its low heats of solution and sublimation, 10 and 37 kcal., represents one extreme case. NaF, with the values 26 and 61 kcal., respectively, represents another extreme case, the high values resulting from the small size of both Na$^+$ and F$^-$. The low heat values for CsF may be connected with the polarization of the large Cs$^+$ by the small F$^-$. The heat of solution of sodium halides in sodium metal increases from the chloride (20 kcal.) to the iodide (28 kcal.), even though the heat of sublimation of the salt decreases from 48 to 43 kcal. More energy should be required to "substitute" anions of increasing size for electrons in a metal of comparatively high cohesive energy such as sodium (small atoms or ions, $\Delta H_v = 23$ kcal.). The "substitution" of different anions for electrons in cesium, a metal of much lower cohesive energy ($\Delta H_v = 16.3$ kcal.) should require less energy, and the energy requirement should not be very much different for different anions. The cohesive energy of the solid cesium salt which decreases slightly from chloride to iodide ($\Delta H_s = 39$ and 38 kcal., respectively), should then be a more important factor in determining the heat of solution. In accordance with this notion, the heat of solution was found to decrease slightly from 22 ± 2 for CsCl to 18 ± 1 kcal. for CsI.

Introduction

New techniques were recently developed for the determination of phase equilibria in systems composed of liquid alkali metals and their halides.[3] It was found necessary to isolate a sample of the equilibrated liquid phases at the temperature of equilibration, because these phases changed rapidly in composition even on fast cooling. Approximate minimum temperatures of miscibility in all proportions (consolute temperatures) of liquid sodium metal with its fused halides were thus obtained by extrapolation from measurements at slightly lower temperatures. The high solubilities of the metal in the fused salts were seemingly in contradiction to a theory[4] based on measurements with multivalent metal-halide systems. This apparent contradiction was explained by considering the high fugacity of the alkali metal at temperatures where the multivalent metals have low fugacities.

Three principal topics are discussed in the present report: (1) the direct experimental demonstration of miscibility in all proportions of an alkali metal with its salts in the liquid state, (2) the effect upon miscibility of variation of the cation in systems containing the same anion, as in the series NaF–Na, KF–K and CsF–Cs, and (3) a comparison of the effect of variation of the halide ion in systems containing the same cation, when this cation is a large one such as Cs$^+$ in the series CsF–Cs, CsCl–Cs and CsI–Cs, or a small one such as Na$^+$ as in the series of the systems of sodium metal with its halides studied previously.[3]

Experimental

Methods used for the determination of equilibrium compositions of the liquid phases and for obtaining cooling curves were the same as previously reported.[3] In fact, the ball-check valve capsule was developed in studying the KF–K system. For the cesium systems the decantation method was used exclusively since no two-liquid phase region was found. Because of the high cost of materials, especially the cesium metal, the diameter of the capsule was reduced from 0.75 in., employed with the sodium and potassium systems, to 0.25 in. Since it was necessary in these determinations to know whether if any solid salt remained under equilibration conditions as well as whether the liquid portion of the system was homogeneous, a further slight modification of the decantation type of capsule was made. The solid salt was placed above a stainless steel wire gauze in the upper part of the tube. After equilibration, the furnace was tilted so as to drain the liquid from any remaining salt and then tilted to another position in order to separate the liquid into two portions by decantation. In cases where no solid phase was found undissolved above the wire gauze, both of these portions were analyzed and identity of composition was taken to indicate the presence of only one liquid phase.

The potassium metal contained 0.27% sodium, by spectrographic analysis, and 0.3% oxygen, determined[5] using the Wurtz reaction. Anhydrous reagent grade potassium fluoride and C.P. cesium chloride were treated in the same manner as described previously[3] for sodium salts. Cesium iodide was purchased in large, optically and chemically pure crystal fragments. Cesium fluoride was prepared by treating cesium chloride with aqueous silver fluoride obtained by dissolving silver carbonate in hydrofluoric acid. Dehydration and fusion of cesium fluoride and potassium fluoride were carried out in platinum containers.

The cesium metal was pure except for traces (0.01%) of rubidium and potassium. Its transfer from the glass ampoule, containing two grams, to the test capsule was accomplished in the glass apparatus shown in Fig. 1. The ampoule was opened under hexane and placed in the upper part of the assembly with an atmosphere of argon above it. After pumping off the hexane the cesium metal, again under argon, was allowed to melt and drop into the stainless steel capsule containing the desired quantity of salt. The capsule was then connected through a rubber stopper and a glass tube to a vacuum system to remove the argon. After evacuation, the glass tube was sealed off and the upper part of the stainless steel capsule was crimped in a vise, sawed

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(1) Work performed for the U. S. Atomic Energy Commission. Presented in part before the Division of Physical and Inorganic Chemistry of the American Chemical Society, Kansas City, Mo., March 23–April 1, 1954.

(2) Consultant from the Department of Chemistry, University of Tennessee.

(3) M. A. Bredig, J. W. Johnson and Wm. T. Smith, Jr., This Journal, **77**, 307 (1955).

(4) D. Cubicciotti and C. Thurmond, *ibid.*, **71**, 2149 (1949); D. Cubicciotti, *ibid.*, **71**, 4119 (1949); *ibid.*, **74**, 1198 (1952).

(5) J. C. White, W. J. Ross and Robert Rowan, Jr., *Anal. Chem.*, **26**, 210 (1954).

off above the crimp and Heliarc-welded to complete the loading operation.

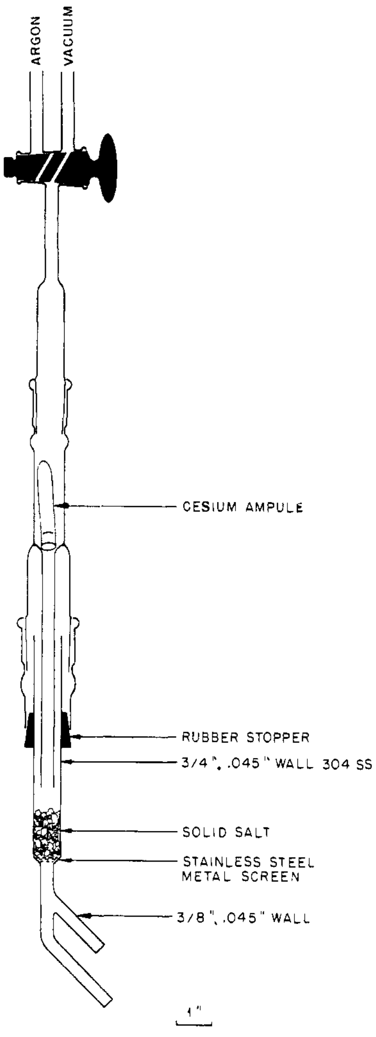

Fig. 1.—Equilibration tube and loading apparatus for use with cesium metal.

Results and Discussion

Tables I and II contain the results of solubility determinations in the systems KF–K, CsF–Cs, CsCl–Cs and CsI–Cs. In Fig. 2 the results for the KF–K system are plotted. Figure 3 affords a comparison of the three fluoride systems, NaF–Na, KF–K and CsF–Cs. Figure 4 is a plot of the logarithm of salt solubility in liquid metal *vs.* the reciprocal of the absolute temperature for all of the nine alkali metal–alkali halide systems investigated thus far.[6]

In contrast to the sodium systems, it was possible with these systems to measure experimentally the solubilities up to complete miscibility. This is largely due to the lower temperatures required here. For instance, the consolute temperature in the KF–K system, *i.e.*, the temperature at which the solubility curve of the metal in the fused salt meets the solubility curve of the salt in the liquid metal, was found to be 910° which is only 50° above the melting point of the salt. In the experiments run above 910° and listed in Table I, the composition of the samples turned out to be identical with that of the charge. Thus, the existence of only one liquid phase in this temperature range was directly demonstrated.

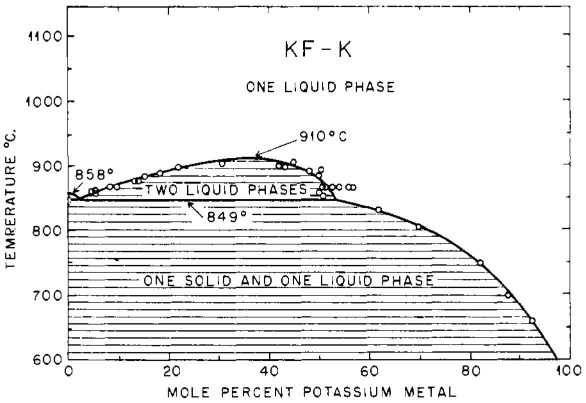

Fig. 2.—The potassium fluoride–potassium metal system.

TABLE I

EQUILIBRIUM PHASE COMPOSITIONS IN THE SYSTEM KF–K

Phases present	Temp., °C.	Mole % KF Charge	Liq. salt-rich phase	Liq. metal-rich phase	Experimental method
Solid salt and one liquid	658	54.7		7.6	Ball-check valve capsule
	697	29.3		12.3	Decantation
	750	47.9		17.7	Ball-check valve capsule
	803	48.7		30.4	Decantation
	832	51.0		38.4	Ball-check valve capsule
	858	100.0	100.0		Cooling curve
Solid salt and two liquids	849	81.4	(97.5)[a]	(45.0)	
Two liquids	853	56.7		48.9	Decantation
	862	75.8	94.0		Ball-check valve capsule
	862	71.1	94.8	49.6	
	863	71.3	93.7		
	865	56.3	92.6	45 0	
	865	57.3	90.3	42.0	
	865	55.5		49.0	
	865	50.2		49.3	
	865	51.6		47.0	
	865	59.4		43.1	Decantation
	877	67.5	85.6		Ball-check valve capsule
	877	71.6	85.2		
	881	67.8	84.4	50.8	
	886	67.6	82.0	49.5	
	886	68.4		51.9	
	894	67.0	78.3	56.0	
	894	57.8		57.6	Decantation
	905	64.7	69.5	54.0	Ball-check valve capsule
Consolute	(910)		(63)	(63)	
One liquid	948	76.0	76.7		Ball-check valve capsule
	948	74.7	73.5		
	975	60.0	59.9		
	980	30.0	30.0	32.0	
	1060	60.0	58.5	58.2	

[a] Values in parentheses obtained by interpolation.

There is considerably greater scattering of experimental points in the KF–K system for the less dense metal-rich liquid phase than for the more dense salt-rich liquid phase (Fig. 2). It is possible that due to a comparatively small difference in density of the phases in this case, and to a possibly considerable interfacial tension, droplets of the heavier salt-rich phase were sometimes floating on top of the metal phase.

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(6) Five experimental points on the KCl–K system have been taken from measurements by J. W. Johnson of this Laboratory, which are to be reported in another connection later.

Table II

Equilibrium Phase Compositions in the Cesium Halide–Cesium Systems

System	Phases present	Temp., °C.	Mole % salt: Charge (approx.)	Mole % salt: Remainder of filtrate	Mole % salt: Decantate from filtrate	Exptl. method
CsF–Cs	Solid salt and one liquid	349	42		3.9	Decant.; no filtration
		452	46		11.4	No decant; no filtr.
		527	61		22.1	Decant.; no filtration
		599	86		36.3	
		640	57		50.1	
		662	84		63.3	
		671	86		74.6	
		692	94[c]			Cooling curve
		703[b]	100[c]			
CsCl–Cs	Solid salt and one liquid	486	60		5.9	Decantation from filtrate
		513	35		8.6	
		549	48		15.5	
		601	53		32.4	
		611	76		56.1	
		621	86		78.0	
	One liquid	620	69	70.0	67.2	
		622	70	70.1	72.8	
		626	91	86.5	86.1	
		630	85		85.7	
		632	75	76.7	76.2	
	Solid and liquid salt	640	100			Cooling curve
CsI–Cs	Solid salt and one liquid	399	37		1.7	Decantation from filtrate
		450	34		4.3	
		549	49		19.0	
		571	61		36.6	
		580	67	56.1[a]		
		592	90		72.5	
		609	93			Cooling curve
	One liquid	580	43	43.4		Decantation from filtrate
		580	43	41.9	42.0	
		597	72	73.0	73.4	
		598	60	58.2	58.0	
	Solid and liquid salt	626	100[c]			Cooling curve

[a] Since no decantate was obtained, this value was accepted as the solubility value. [b] Incomplete removal of hydrogen fluoride may possibly have accounted for the somewhat lower values 680 and 684° obtained for the melting point of this salt by F. M. Jaeger, *Z. anorg. Chem.*, **101**, 193 (1917), and H. Wartenberg and H. Schulz, *Z. Elektrochem.*, **27**, 568 (1921). The value 703° reported here was obtained on samples from which hydrogen fluoride had been removed by evacuation and flushing with argon at 600° until no acidity was detectable in the gas stream. This value is in good agreement with 705° reported by O. Schmitz-Dumont and co-workers, *Z. anorg. Chem.*, **252**, 329 (1944); **271**, 347 (1953). [c] Determined accurately by analysis.

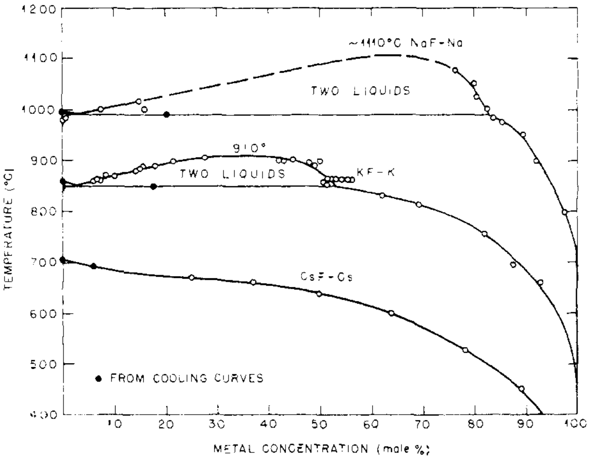

Fig. 3.—Comparison of the three systems NaF–Na, KF–K, CsF–Cs.

The data illustrate a striking effect on the solubility of the solid salt in the liquid metal produced by the variation of the cation in both the metal and the halide: increasing the atomic number of the metallic element from sodium to potassium and cesium leads to very large increases in solubility of the solid salt in the liquid metal. For instance, at 550° the solubilities of the halides of sodium, potassium and cesium in the metals range from 0.1 to 0.2, 1 to 2, and 15 to 25 mole %, respectively (Tables I and II and Fig. 4). Largely as a consequence of this trend, the concentration–temperature area of the diagram in which two liquid phases are in equilibrium shrinks rapidly with increasing atomic number of the metal. Indeed, the experimental results show that two liquid phases no longer coexist in the cesium systems as they still do in the KF–K system. Only solid cesium salts and one liquid solution were ever found in equilibrium. Thus, increasing additions of cesium metal to the salt lower the melting point continuously. An unbroken, "S" shaped liquidus curve (Fig. 3) connects the melting point of the salt with the eutectic point which can be shown by extrapolation of the log s *vs.* $1/T$ plot to practically coincide with the melting point of the metal. For CsF, *e.g.*, the solubility at 30° is less than 0.001 mole %.

The solid phases, though essentially pure salt, contained a small amount of cesium metal in solid solution. This was indicated by the deep purple-blue-black color of the undissolved, quenched salt crystals which had been equilibrated with the metal solutions. The color, on dissolving these crystals, was found to have penetrated them. In the case of the KF–K system the color of the solid salt phase is light yellow.

Partial heats of solution, at saturation, of the salts in the liquid metals were calculated from the slopes of the logarithm of the solubility (mole %) *vs.* $1/T$ plots. This relation may be assumed to be approximately valid in the region where the composition of the solid is almost that of the pure salt and where the plotted data give a straight line. In this manner the heat of solution of cesium fluoride was found to be 10 ± 0.5 kcal. compared with 22 ± 2 and 18 ± 1 for the chloride and iodide, respectively. It seems significant that cesium fluoride stands out with its low heat of solution as it does with its low heat of sublimation, $\Delta H_s = 36.8$ kcal., as against 39.3 and 38.4, respectively,[7] and that there is little difference between the chloride and iodide. In the sodium systems the fluoride has also been found[3] to stand apart from the others, but by a high rather than a low value of the heat of solution (26 kcal. for the fluoride compared with 20 ± 3 and 28 ± 2 for the chloride and iodide). An explanation may be based on the exceptionally high cohesive energy of the fluoride (heat of sublimation, $\Delta H_s = 61$ kcal.) due to the relatively small sizes of both Na^+ and F^- and on the increasing amount of energy required to "substitute" a larger anion ($R_{I^-} = 2.20$ Å. as compared with $R_{Cl^-} = 1.80$ Å.) for an electron in the liquid metal (or a

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(7) Leo Brewer, in "The Chemistry and Metallurgy of Miscellaneous Materials. Thermodynamics," Vol. IV-19B, of National Nuclear Energy Series, McGraw-Hill Book Co., New York, N. Y., 1950.

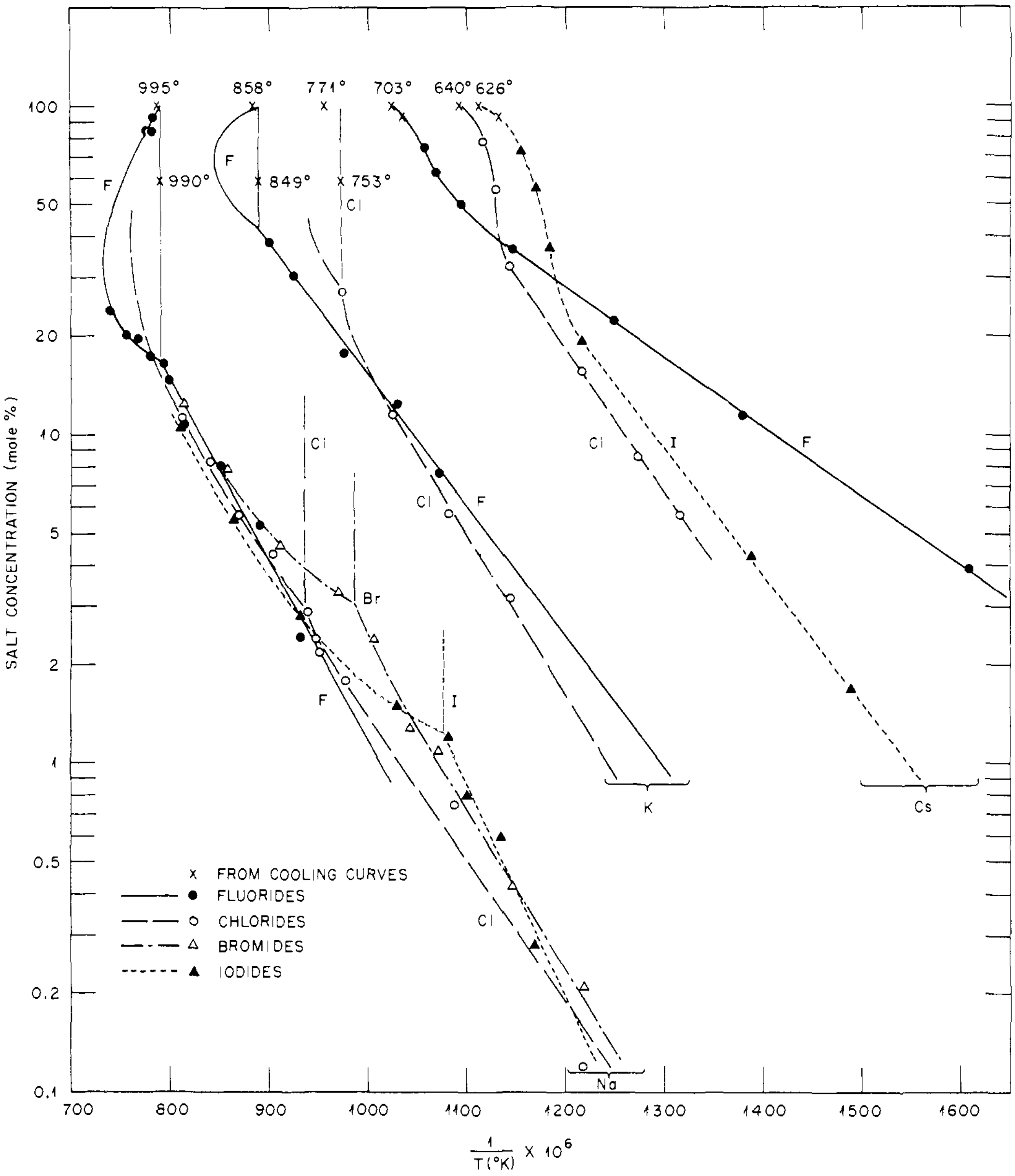

Fig. 4.—The solubility of solid alkali halides in alkali metals.

larger molecule MX for an M atom). In comparison with the differences in "substitution energy" the differences in cohesive energy of the salts (ΔH_s: 48 (NaCl), 44 (NaBr), 43 kcal. (NaI)) appear to be minor except in the case of sodium fluoride (61 kcal.). Applying the same principles to the cesium systems we find that the exceptionally low cohesive energy of the fluoride (ΔH_s = 36.8 kcal.) leads to a low heat of solution. Also, a smaller difference in the energy required for substituting anions of different sizes for electrons may be expected with cesium, a metal of large atoms or ions (R_{Cs^+} = 1.69 Å.) and of low cohesive energy (ΔH_v = 16.3 kcal.), than with the more cohesive sodium (R_{Na^+} = 0.98 Å., ΔH_v = 23.1 kcal.). Thus in the cesium systems the small difference in the "substitution energy" and the relative constancy or small decrease of the cohesive energy of the solid salt in going from the chloride[8] to the iodide (ΔH_s = 39.3 and 38.4 kcal. respectively) is reflected in the—rather slight—decrease of the heat of solution from 22 ± 2 to 18 ± 1 kcal. In going from F^- (R = 1.33 Å.) to the Cl^- (R = 1.80 Å.) there may be a significant contribution to the increase in heat of solution resulting from an increase in "substitution energy" even in the case of cesium. This contribution *adds* to the effect of increased cohesive energy of the chloride and leads to an even greater difference between the chloride and fluoride (22 and 10 kcal.). In the case of the sodium systems it *counteracts* the effect of the lower cohesive energy of the chloride and therefore diminishes the difference between the heats of solution of the fluoride and chloride (26 and 20 kcal.).

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(8) No attempt was made to determine the small solubility of the low-temperature form of CsCl, which is isomorphous with CsI.

Heats of sublimation rather than of vaporization of the salts are used because *solid* salt solubility is the subject of this particular discussion. However, the use of heats of vaporization for the salts as well as for the metals would not have altered the results. Lattice energies were not considered because the ions of the salts in the liquid metal solutions are not thought to be separated by intervening solvent atoms. When the cations of the metal and the salt are identical, as in the two-component systems dealt with here, separation of the compensating positive charge from the first sphere of coördination of a negative ion must be a very minor effect. In three component liquid solutions containing two different metal ions and one anion, the extent of such separation should largely depend on the relative stability of the halides of the two metals.

The discussion above does not include terms for exothermic processes resulting from the attraction between solute and solvent molecules or atoms. For this and similar reasons it is perhaps somewhat surprising, and may even be fortuitous, that the qualitative considerations fit the experimental observations as well as they do.

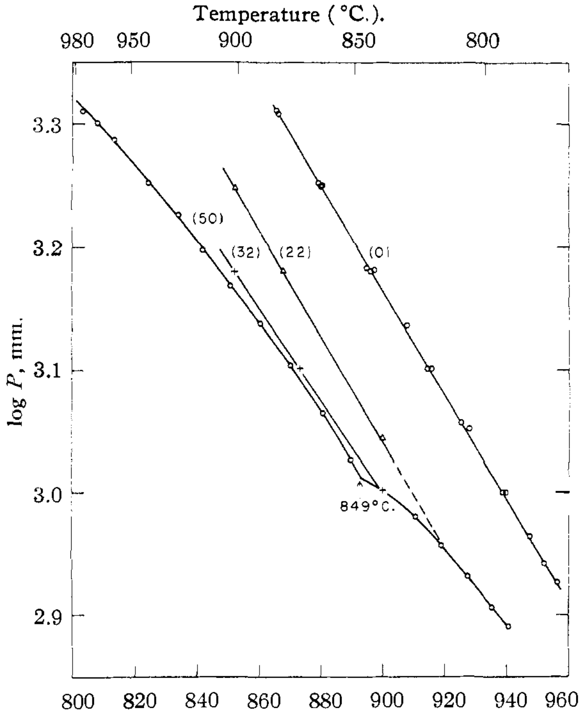

Fig. 5.—Vapor pressures of potassium fluoride–potassium mixtures (numbers designate mole % KF).

It is possible that the CsI–Cs system among all metal–metal halide systems shows the lowest temperature of complete miscibility of any liquid salt with any liquid metal. It may also be predicted by extrapolation beyond the sodium systems that the lithium systems, especially the iodide, will show the largest temperature–concentration area of immiscibility of two liquids of all the alkali metal–alkali halide systems. This should be largely due to the very much higher cohesive energy of lithium metal (ΔH_v = 32.5 kcal.). Experimental work on these systems has been started.

Vapor Pressure Measurements.—The unexpectedly high solubilities of salts in liquid metals, found in the early stages of this investigation, prompted the measurement of some physical property of the solutions which should vary continuously with composition. That is, it was feared that a colloidal suspension or mechanical mixture was being sampled instead of a solution. Since the metals have significant vapor pressures at the temperatures of the solubility determinations and the salts have negligible vapor pressures at these temperatures, the variation of vapor pressure with concentration of the solution was chosen as the most direct proof of a lowering of the activity of the metal as a solvent. The vapor pressures of solutions of several concentrations of potassium fluoride in potassium were measured over the range 1–2 atm. (see Fig. 5). While the vapor pressure lowering was not simply related to the mole fraction of fluoride there was a progressive lowering observed with charges containing 0, 22, 32 and 50 mole % salt. The deviations (up to 15%) from calculated vapor pressures may have been due to lack of ideality of the solutions and to "hold up" of the volatile solvent in the colder parts of the vapor pressure measuring device. The break in the curve for the 50 mole % mixture (Fig. 5) occurs at 849° and checks exactly with the monotectic temperature determined from cooling curves (Fig. 2). The vapor pressure measurements were made in a stainless steel container by observing boiling temperatures as a function of the pressure of an inert gas (argon) in contact with the charge. The equipment is being modified to extend the range of pressure measurements and to allow sampling of the solutions. This equipment will be described in a later paper, dealing with the determination of the activities in these systems.

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