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HIGH PRESSURE PHASE STUDIES ON SODIUM, POTASSIUM,
RUBIDIUM AND CESIUM METALS AND ON SODIUM-POTASSIUM ALLOYS

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High Pressure Phase Studies on Sodium, Potassium,
Rubidium and Cesium Metals and on Sodium-Potassium Alloys

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The solid-liquid phase diagrams are investigated to 60 kbars for elemental sodium, potassium, rubidium, and cesium, and for various sodium-potassium alloys. The data for Na, K, and Rb are in agreement with earlier workers. Our Cs melting points, however, are considerably higher than the literature values. In the sodium-potassium alloy system, the peritectic and eutectic halts intersect at 35 kbars and 343°C. Above this pressure, two halts are observed, one of which increases while the other decreases with increasing pressure to 55 kbars where it abruptly starts increasing again. Melting points in the 0.6-0.8 mole fraction potassium range indicate that an NaK_2 intermetallic compound may form at high pressures.

Considerable data are available in the literature on the effect of pressure on the alkali metals. Bridgman¹ measured the melting curves of the

¹P. W. Bridgman, Phys. Rev., 27, 69 (1926).

five alkali metals to pressures ranging from 4 to 12 kbars. Ponyatowskii² ex-

²E. G. Ponyatowskii, Metals Metallog. (USSR) (English Translation) Phys., 11, 146 (1962).

tended the phase diagram for lithium and sodium to 30 kbars. Later the diagrams

for all five metals were extended to 50 kbars by Newton³, et al. and by

³R. B. Newton, A. Jayaraman, and G. C. Kennedy, J. Geophys. Res., 67, 2559 (1962).

Kennedy⁴, et al. Bundy⁵ measured the phase diagram for rubidium to 150 kbars,

⁴G. C. Kennedy, A. Jayaraman, and R. C. Newton, Phys. Rev., 126, 1363 (1962).

⁵F. P. Bundy, Phys. Rev., 115, 274 (1959).

and Jayaraman⁶ extended the cesium diagram to 55 kbars. Hall⁷, et al. have

⁶A. Jayaraman, R. C. Newton, and J. M. McConough, Phys. Rev., 159, 527 (1967).

⁷H. T. Hall, L. Merrill, and J. D. Barnett, Science, 146, 1297 (1964).

studied this latter system at high pressures by x-ray diffraction. Finally, Luedemann,⁸ et al. have extended the Li, Na, K, and Rb diagrams to 80 kbars. Very

⁸H. P. Luedemann and G. C. Kennedy, J. Geophys. Res., 73, 2795 (1968).

little information is available in the literature, however, on the effect of pressure on the phase properties of alkali metal alloys. Kean⁹ determined the

⁹C. H. Kean, Phys. Rev., 55, 750 (1939).

solid-liquid phase diagram for the Na-K binary system up to a pressure of ten kbars. He found that the composition of the eutectic varied with pressure, but stated that the peritectic composition did not change. His phase diagram, however, does show a slight change in the peritectic composition.

Newton³, et al. made thermal measurements on an Na-K alloy with the atmospheric pressure eutectic composition. He traced the eutectic halt up to about 30 kbars where it faded out.

Since the data available are so limited, we felt it desirable to further investigate the Na-K, binary phase diagram at high pressures. Of special interest was the change in composition and temperature of the invariant points in the system. In view of Newton's³ observation that the eutectic disappeared at about 30 kbars, the question arises as to whether gross changes in the phase diagram of the Na-K system might be occurring at elevated pressures (above 30 kbars). Finally, we were interested in seeing if new compounds might form at high pressures.

EXPERIMENTAL

Summary of Methods

Samples were prepared in an inert atmosphere glove box and encapsulated in a polyethylene tube. This capsule was inserted in a graphite tube which was placed in the center of a pyrophyllite tetrahedron and subjected to pressures up to 55 kbars in a tetrahedral anvil press.

At fixed pressures, time-temperature heating and cooling curves were used to determine invariant points and melting points. Temperatures were measured with a thermocouple immersed directly in the alloy sample. Temperature changes were obtained by using the graphite cylinder as a heater.

Pressure Apparatus

The high pressure studies were carried out in a tetrahedral anvil press, designated T-6 at Brigham Young University. The press was designed by H. T.

Hall.^{10,11} It consists of four hydraulic rams with eight inch diameter pistons

¹⁰H. T. Hall, Rev. Sci. Instr., 29, 267 (1958).

¹¹H. T. Hall, Rev. Sci. Instr., 33, 1278 (1962).

capable of exerting a maximum thrust of 200 tons each. Cemented tungsten carbide anvils in front of the rams are advanced over a distance of about two inches as they close on the triangular faces of a pyrophyllite tetrahedron. Samples to be studied are imbedded in the pyrophyllite. The space between adjacent anvils allows for extrusion of pyrophyllite to form a gasket. The thermocouple leads from the sample are brought out through this gasket. This gasket also insulates the anvils from one another so that they can be used as contacts for the sample heater imbedded in the pyrophyllite tetrahedron.

Sample Preparation

The alkali metals used were the same as have been used in previous atmospheric pressure phase equilibria work.^{12,13,14} Their purity is described

¹²J. B. Ott, J. R. Goates, D. R. Anderson, and H. T. Hall, Jr., Trans. Faraday Soc., 65, 2870 (1969)

¹³J. R. Goates, J. B. Ott, and C. C. Hsu, Trans. Faraday Soc., 66, 25 (1970).

¹⁴J. B. Ott, J. R. Goates, and D. E. Oyler (Submitted to Trans. Faraday Soc.).

in the literature. In general, each of the alkali metals is at least 99.9% pure with less than 50 ppm of other alkali metals as impurities. The bismuth used in calibrating the press by resistance measurements was at least 99.5 percent pure. The mercury, which was also used for calibration is triply distilled and as such is at least 99.99% pure.

Liquid samples of the alloy mixtures were prepared and encapsulated in a Vacuum Atmosphere Corporation inert atmosphere glove box. Circulation of the argon atmosphere through a purification train kept oxygen and water vapor concentration at <1 ppm. Under these conditions, the liquid alloys showed no oxide formation after several hours in the box. Samples were prepared by weighing the alkali metals inside the glove box on a top-loading Mettler P-160 single pan balance, which is accurate to ± 0.001 g. The samples were weighed into a nickel crucible and melted to form a uniform liquid solution, which was then transferred to a capsule.

The capsule was made by sealing the ends of 0.138 in. O.D. by 0.106 in. I.D. polyethylene tubing. When prepared the capsules were $3/8$ inch in length. A thermocouple is sealed in one end and a small hole made in the other. The alloy mixture was injected into the capsule through this hole, after which the hole was sealed with a warm soldering iron. Polyethylene forms a very adequate encapsulation material for these experiments. There was no noticeable decomposition of the plastic at pressures up to 55 kbars and temperatures up to 350°C .

Pressure Calibration

Thermal measurements were made on mercury at the melting temperature to obtain a pressure scale in the press. Mercury has recently been proposed as a calibration standard.¹⁵ The variation of the melting point with pressure

¹⁵V. S. Bogdanov "On the Application of Mercury Melting Curve for Accurate High Pressure Measurements," Symposium on the Accurate Characterization of High Pressure Environment, U. S. Department of Commerce, NBS, Gaithersburg, Maryland, Oct. 14-18, 1968.

has been well investigated; and since the method for determining the melting

point duplicates the conditions under which our experimental measurements on the alkali metals and their alloys were made, the choice of the Hg melting point as a calibration standard was particularly advantageous.

Klement,¹⁶ et al. have studied the phase transformations of mercury at

¹⁶W. Klement Jr., A. Jayaraman, and G. C. Kennedy, Phys. Rev., 131, 1 (1963).

pressures up to 65 ± 2 kbars. They plotted their data along with that of five other similar but independent investigations. This composite fusion curve was used by us as a primary pressure calibration standard. We also obtained the Bi (I-II) transition calibration point by resistance measurements. The value for this transition of 26.5 kbars¹⁷ fits on our mercury

¹⁷R. N. Jeffrey, J. Appl. Phys., 37, 3172 (1966).

calibration curve to within ± 1 kbar. As a result of these calibration measurements we consider our pressure calibration to be accurate to within ± 1 kbar in the low pressure region (< 40 kbars) and ± 2 kbars at pressures above 40 kbars.

Temperature Scale

Temperatures were measured with a chromel-alumel thermocouple. This thermocouple was chosen because it is known to have a small pressure coefficient. Hanneman,¹⁸ et al. have given a critical review of the pressure effect just

¹⁸R. E. Hanneman, et al., "A Critical Review of the Effect of Pressure on Thermocouple EMF's," A Symposium on the Accurate Characterization of the High Pressure Environment, U. S. Dept. of Commerce, NBS, Gaithersburg, Maryland, Oct. 14-18, 1968.

mentioned and suggest a correction of about 1°C at 40 kbars and 1000°C . Since the maximum temperature we used is 350°C and the correction is uncertain to $\pm 25\%$, we neglected the correction in our work. The thermocouple was calibrated at atmospheric pressure to $\pm 0.2^{\circ}\text{C}$. We consider this calibration to be accurate to $\pm 1^{\circ}\text{C}$ over the pressure and temperature ranges used in these measurements.

EXPERIMENTAL RESULTS

Two different techniques were employed to obtain the time-temperature cooling and warming curves necessary to determine the melting and invariant points. A comparatively slow, but uniform heating or cooling was obtained by programming the D.C. power supply that supplied electrical energy to the graphite heater which surrounds the sample. A linearly increasing signal from an integrating operational amplifier was fed into the power supply causing the output voltage to increase linearly. With this source, the temperature range of interest could be swept through in any time period of interest. Temperature readings from the thermocouple were followed with an x-y recorder. The invariant points and melting points of the pure metals were obtained in this manner. However, it was not possible to obtain reliable melting points of the alloys with this technique. Evidently the heat leak from the sample heater into the anvils of the press is so large that the small changes in the slope of the cooling and warming curves on melting goes unnoticed. This difficulty was at least partially overcome by heating these samples rapidly. An A.C. powerstat was set at a voltage to give a final temperature above the melting point. The switch was then turned on and the temperature range was swept through in about 10 seconds. Turning off the switch then caused cooling back through the range in about 6 seconds. Temperature readings were again followed with the x-y recorder. This rapid cooling and warming

gave better breaks at the melting point, but more supercooling and possibility for nonequilibrium.

Pure Alkali Metals: The melting points of high purity samples of Na, K, Rb, and Cs are summarized in Table 1 and Figure 1. We estimate that these invariant points, which were obtained by slow cooling and warming are accurate to $\pm 1^\circ\text{C}$. The results for Na, K, and Rb differ at some pressures by as much as $\pm 5^\circ\text{C}$. or ± 1 kbar from the recent results of other workers^{3,4}. Most of the difference can be explained from the methods used to arrive at the melting points. Luedemann⁸ et al. claimed that their melting and freezing points were displaced from one another by about 5° . They took the onset of the thermal arrest in melting and the last trace of the arrest in freezing and calculated an average temperature. In our work, the thermal arrest in melting was very sharp and reproducible. We used this value as the melting point since supercooling was considered to be too great in the cooling curves to allow for recovery of the halt to an equilibrium value. The biggest discrepancy is in the melting curve for Cs. At pressures above 30 kbars, our melting points are as much as 45° (or 6 kbars) higher than the data of Kennedy⁴. This discrepancy may be caused by possible lower purity of the cesium used by Kennedy in his study.

Sodium-Potassium System: Average values for the invariant points (eutectic and peritectic) for this system are tabulated in Table 2. Agreement at different compositions between the values for the halts is good at pressures below 35 kbars. The average standard deviation over all the compositions is $\pm 2^\circ\text{K}$. Above 35 kbars, the average standard deviation becomes ± 4 kbars. The reactions causing the halts in this region are much more sluggish; and, hence, harder to keep at equilibrium. We noted, as did Newton,⁴ that the eutectic halt disappeared at 30 kbars for an alloy with the eutectic composition. We

concluded that this disappearance results simply from a shift in eutectic composition toward lower potassium concentrations. Evidence for this is the fact that the eutectic halt disappeared at successively lower pressures as the alloy became richer in potassium.

Figure 1 shows a graph of the average values of the change of the invariant temperature with pressure. The interesting feature of the diagram is the intersection of the eutectic and peritectic halts at about 35 kbars. Two halts were still apparent in the system above 35 kbars. The behavior of the system however is very different in this region. The halts although more sluggish, are much stronger with the lengths increasing by as much as a factor of ten over the values below the intersection. The lower of the two curves above 35 kbars is especially interesting in that the halt decreases with increasing pressure up to about 55 kbars where the halt temperature abruptly starts increasing again. This behavior is similar to that found in elemental cesium.

In determining melting points, we found it very difficult to obtain reliable values (even with rapid cooling and warming techniques) in the composition range between the peritectic and eutectic. The break in the curve in this region was too gradual to obtain a good value. For this reason, we have not attempted to obtain a complete phase diagram. Better values were obtained in potassium rich alloys. Figure 2 shows values for the melting points in this composition region. The data are interesting in that they suggest the formation of an NaK_2 intermetallic compound at high pressures. An independent x-ray study at high pressures is planned to see if such a compound can be identified.

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at Brigham Young University, for letting us use the high pressure equipment and for many helpful suggestions and discussions throughout the course of the measurements.

TABLE 1

Melting Points of Alkali Metals

<u>Pressure,</u> <u>kbars</u>	<u>Temperature,</u> <u>°K</u>	<u>Pressure,</u> <u>kbars</u>	<u>Temperature,</u> <u>°K</u>	<u>Pressure,</u> <u>kbars</u>	<u>Temperature,</u> <u>°K</u>
<u>Sodium</u>					
0	371.05 ^a	30.0	515	50.5	556
6.3	427	34.5	524	52.8	565
12.8	460	38.8	533	54.5	565
18.5	482	42.3	542	56.0	569
23.0	498	45.5	548	57.3	572
27.8	510	48.3	555		
<u>Potassium</u>					
0	336.86 ^a	32.3	522	51.5	547
6.3	418	36.8	525	53.8	551
12.8	459	40.5	532	55.3	551
18.5	482	44.0	538	56.8	554
23.0	499	46.8	543	57.8	555
27.8	511	49.5	544		
<u>Rubidium</u>					
0	312.45 ^a	23.0	493	46.8	540
6.3	405	27.8	508	51.5	546
12.8	451	32.3	518	55.3	553
18.5	475	40.5	530		
<u>Cesium</u>					
0	301.59 ^a	23.0	469	49.5	410
6.3	406	27.8	467	51.5	382
9.5	432	32.3	473	53.8	368
12.8	448	36.8	470	55.3	377
15.5	458	40.5	463	56.8	410
18.5	467	44.0	450	57.8	432
20.8	469	46.8	432		

a - Value obtained at atmospheric pressure outside the press.

TABLE 2

Effect of Pressure on the Invariant Points
in the Sodium-Potassium System

Pressure, kbars	Eutectic Temperature, °K	Peritectic Temperature, °K	Pressure, kbars	Upper ^c Invariant Temperature, °K	Lower ^c Invariant Temperature, °K
0	276.51 ^a	280.06	36.8	346	344
6.3	- - - ^b	312	38.8	353	344
9.5	302	321	40.5	356	341
12.8	307	325	44.0	365	336
15.5	314	330	46.8	375	330
18.5	318	334	49.5	382	325
20.8	323	337	51.5	389	319
23.0	327	338	53.8	396	313
25.3	331	341	55.3	397	316
27.8	334	342	56.8	406	324
30.0	337	343	57.3	406	322
32.3	339	344	57.8	411	331
34.5	342	344			

a - Value obtained at atmospheric pressure outside the press.

b - Value below room temperature.

c - Invariant points at pressures above the peritectic-eutectic intersection.

Fig. 1--Invariant points in the sodium-potassium alloy system

Fig. 2—Melting points as a function of pressure in the sodium-potassium alloy system.