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High-Pressure Phase Studies on Sodium–Potassium Alloys

D. Ray Anderson

J. Bevan Ott
bevan_ott@byu.edu

Rex J. Goates

H. Tracy Hall

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and

$$\Delta^{(2)}\eta = \frac{1}{2}(kT) [(\psi_1' + \psi_1'')B_0^{(a)}(2) + (\psi_2 + \psi_2' + \psi_2'')B_1^{(a)}(2) + (\psi_3 + \psi_3' + \psi_3'')B_1^{(b)}(2) + (\psi_4 + \psi_4' + \psi_4'')B_2^{(a)}(2) + (\psi_5 + \psi_5' + \psi_5'')B_2^{(b)}(2)]. \quad (\text{IV.21})$$

These results are also in agreement with those of Levi and McCourt. As in the case of thermal conductivity, the contribution to second order from the terms odd in the angular momentum are zero for rigid, convex models. To fourth order in ϵ we obtain for the saturation contribution to $\Delta\eta$ from $[\mathbf{W}]^{(2)}[\mathbf{\Omega}]^{(1)}$ (coupled only with $[\mathbf{\Omega}]^{(2)}$)

$$(\Delta^{(4)}\eta_{\text{odd}})_{H=\infty} = \frac{3}{2}(b_{28}^2 b_{35}^2 / b_{22}^2 b_{33}^2 b_{55}) \delta^{(2)} \quad (\text{IV.22})$$

where

$$b_{35}T_1^{(5,0)} = \langle \Psi_1^{(1)}(0, 2), J[\Psi_1^{(1)'}(2, 1)] \rangle.$$

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High-Pressure Phase Studies on Sodium-Potassium Alloys

D. RAY ANDERSON, J. BEVAN OTT, J. REX GOATES, AND H. TRACY HALL, JR.

Department of Chemistry, Brigham Young University, Provo, Utah 84601

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The solid-liquid phase diagrams were investigated to 60 kbar for elemental sodium, potassium, and various sodium-potassium alloys. The data for Na and K are in general agreement with those of earlier workers. In the alloy system the temperatures of both the peritectic and eutectic halts increase as the pressure increases, but with different slopes, so that the two invariant points merge at approximately 35 kbar. Above this pressure, two halts are again observed. One increases with increasing pressure, and the other decreases with increasing pressure up to 55 kbar, where it abruptly starts increasing again. Melting points for samples in the 0.6-0.8 mole fraction potassium range indicate that an NaK₂ 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 five alkali metals to pressures ranging from 4 to 12 kbar. Ponyatawskii² extended the phase diagram for lithium and sodium to 30 kbar. Later the diagrams for all five metals were extended to 50 kbar by Newton *et al.*³ and by Kennedy *et al.*⁴ Finally, Luedemann *et al.*⁵ have extended the Li, Na, K, and Rb diagrams to 80 kbar. Very little information is available in the literature, however, on the effect of pressure on the phase properties of alkali metal alloys. Kean⁶ determined the solid-liquid phase diagram for the Na-K binary system up to a pressure of 10 kbar. 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. Newton *et al.*³ made thermal measurements on an Na-K alloy having the atmospheric pressure eutectic composition. They traced the eutectic halt up to about 30 kbar, where it faded out.

Since the data available are limited, we felt it desirable to further investigate the Na-K binary phase diagram at high pressures. Of special interest were the changes in composition and temperature of the invariant points in the system. In view of Newton's³ observation that the eutectic disappeared at about 30 kbar, the question arises as to whether gross changes in the phase diagram of the Na-K system might occur at elevated pressures (above 30 kbar). 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 centered inside a pyrophyllite tetrahedron and then subjected to pressures up to 55 kbar in a tetrahedral anvil press.

At fixed pressures, time-vs-temperature heating and cooling curves were used to determine invariant points and melting points. Temperatures were measured by a thermocouple immersed directly in the alloy sample. Temperature changes were produced 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 Hall.^{7,8} It consists of four hydraulic rams with 8-in.-diam pistons 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 2 in. 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 are brought out from the sample through this gasket, which 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 sodium and potassium used in this study were the same as those used in a previous atmospheric pressure phase equilibria study.⁹ Their purities are described in the literature. The sodium and potassium metals are at least 99.9% pure with <50 ppm total of other alkali metals as impurities. The mercury which was used for calibration was triply distilled. Its purity is better than 99.99%. The bismuth used in checking the calibration of the press by resistance measurements is better than 99.5% pure.

Liquid samples of the Na-K mixtures were prepared within a Vacuum Atmosphere Corporation inert-atmosphere glove box. Circulation of the argon atmosphere through a purification train kept oxygen and water vapor concentrations at <1 ppm. Under these conditions, the liquid alloys showed no oxide formation even 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 $\frac{3}{8}$ in. long. A thermocouple was 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 kbar and temperatures up to 350°C. Periodically, melting points were made at atmospheric pressure on samples recovered from the press after high-temperature and -pressure measurements. The melting points were on the atmospheric pressure melting curve, indicating that the sample did not become contaminated as a result of the measurements.

Pressure Calibration

Melting points vs pressure measurements were made on mercury to obtain a pressure scale for the press. Mercury has recently been proposed as a calibration standard.¹⁰ The variation of melting point with pressure has been well investigated, and since the method for determining the melting point duplicates the conditions under which our experimental measurements on sodium and potassium and its alloys were made, the choice of the mercury melting point as a calibration standard was particularly advantageous.

Klement *et al.*¹¹ have studied the phase transformations of mercury at pressures up to 65 ± 2 kbar. 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. As a check of our calibration curve, we determined the Bi (I-II) transition point by resistance measurements. Using the calibration curve from the Hg melting points, we obtained a value of 25.4 kbar for the Bi point, which is in good agreement with the results of Kennedy¹² (25.410 ± 0.095 kbar) and Heydemann¹³ (25.499 ± 0.060 kbar). As a result of these calibration measurements we consider the accuracy of our pressure calibration to be within ± 1 kbar in the low-pressure region (<40 kbar) and ± 2 kbar at pressures >40 kbar.

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 *et al.*¹⁴ have given a critical review of the pressure effect just mentioned and suggest a correction of about 1°C at 40 kbar and 1000°C. Since the maximum temperature we used was 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.

TABLE I. Melting points of alkali metals.

| Pressure (kbar) | Temperature (°K) | Pressure (kbar) | Temperature (°K) | Pressure (kbar) | Temperature (°K) |
|-----------------|---------------------|-----------------|------------------|-----------------|------------------|
| Sodium | | | | | |
| 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 | | |
| Potassium | | | | | |
| 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 | | |

^a Value obtained at atmospheric pressure outside the press.

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 rate was obtained by programming the dc power supply that supplied electrical energy to the graphite heater which surrounded the sample. A linearly increasing electrical 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 during heating and cooling were followed with an x - y recorder. The invariant points and melting points of the pure sodium and potassium were obtained in this manner. However, it was impossible to obtain reliable melting points of the alloys with this technique. Evidently the heat leak from the sample heater into the

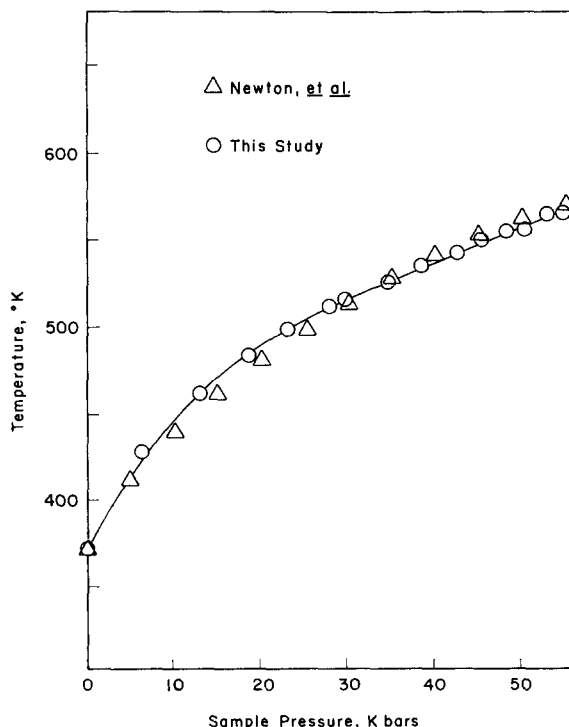


FIG. 1. Melting point of sodium as a function of pressure.

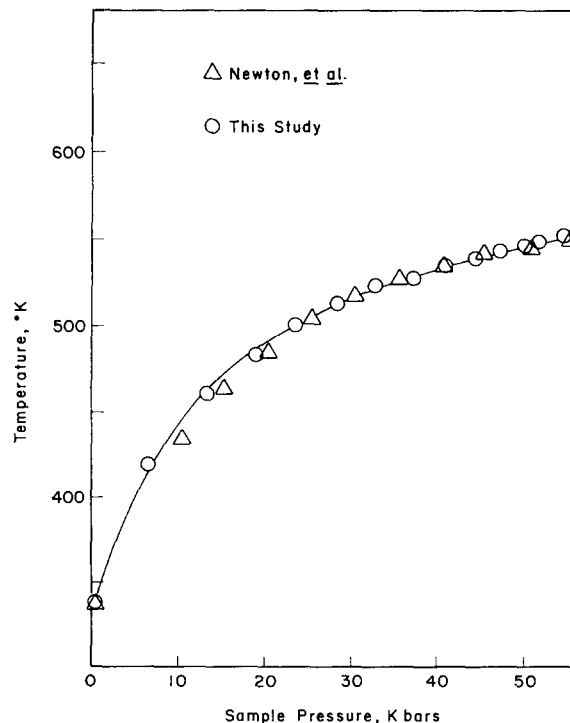


FIG. 2. Melting point of potassium as a function of pressure.

TABLE II. Effect of pressure on the invariant points in the sodium-potassium system.

| Pressure (kbar) | Eutectic temperature (°K) | Peritectic temperature (°K) | Pressure (kbar) | Upper invariant temperature (°K) | Lower invariant temperature (°K) |
|-----------------|---------------------------|-----------------------------|-----------------|----------------------------------|----------------------------------|
| 0 | 260.53 ^a | 280.06 | 36.8 | 346 | 344 |
| 6.3 | ... ^b | 312 | 38.8 | 353 | 344 |
| 9.5 | 300 | 321 | 40.5 | 356 | 341 |
| 12.8 | 306 | 325 | 44.0 | 365 | 336 |
| 15.5 | 313 | 330 | 46.8 | 375 | 330 |
| 18.5 | 319 | 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.

anvils of the press is so large that the small changes in the slope of the cooling and warming curves on melting go unnoticed. This difficulty was at least partially overcome by heating these samples rapidly. An ac powerstat was set at a voltage which would give a final temperature higher than the melting point. The switch was then turned on, and the temperature range was swept through in about 10 sec. Turning off the switch then caused cooling back through the same temperature range in about 6 sec. This rapid cooling and warming gave sharper breaks at the melting point, but resulted in more supercooling and the possibility for non-equilibrium.

Pure Metals

Since the melting points of Na and K as a function of pressure have been measured with concordant results

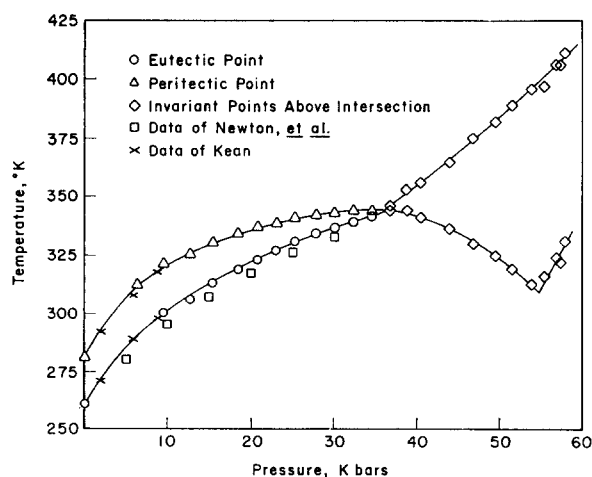


FIG. 3. Temperatures of the invariant points in the Na-K alloy system as a function of pressure.

by several investigators,¹⁻⁵ our measurements of these systems were undertaken principally as a test of our equipment and procedures. Table I summarizes the results of these measurements. As can be seen from Figs. 1 and 2, the data from this study are in general agreement with the recent measurements of Newton *et al.*³ While at some pressures the two sets of data differ by as much as 5°C or 1 kbar, most of this difference can be accounted for by the difference in the methods used in the two studies to arrive at the melting points. Newton *et al.*,³ using differential thermal analysis, reported that their constant pressure melting and freezing points were displaced from one another by about 5°C. To obtain the equilibrium point they averaged the temperature at the onset of the thermal arrest in melting with the temperature at the last trace of the arrest in freezing. In our work, the thermal arrest in melting was very sharp and reproducible. We used this value as the melting point since supercooling was too extensive to allow for recovery of the halt to an equilibrium value.

Sodium-Potassium System

Average values for the invariant point (eutectic and peritectic) for the alloy system are tabulated in Table II. Agreement at different compositions between the values for the halts is good at pressures below 35 kbar. The average standard deviation in this pressure range over all the compositions is ± 2 kbar. Above 35 kbar, the average standard deviation becomes ± 4 kbar. The reactions causing the halts in this higher-pressure region are much more sluggish, and hence harder to keep at equilibrium. We noted, as did Newton,³ that the eutectic halt disappeared at 30 kbar for an alloy of the eutectic composition. We concluded that this dis-

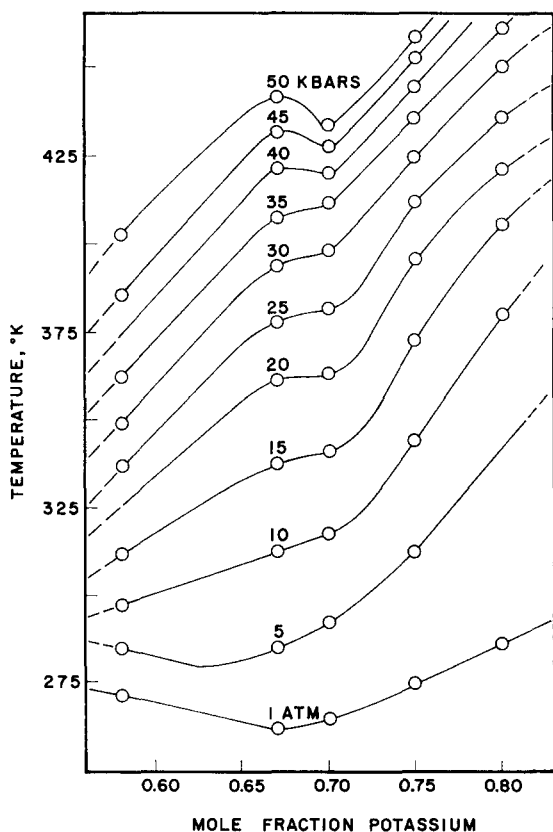


FIG. 4. Melting points as a function of pressure in the sodium-potassium alloy system.

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

Figure 3 is a graph of temperature vs pressure for the two invariant points observed in the system. Data from Kean⁶ and Newton *et al.*³ have been included for comparison. The solid line is drawn through our data alone. The agreement is considered to be satisfactory (± 2 kbar). As with the melting points of the pure metals, the difference in the method of selecting the equilibrium point probably accounts for some of the differences observed. An interesting feature of the diagram is the intersection of the eutectic and peritectic halts at about 35 kbar. Two halts were still apparent in the system above 35 kbar. The behavior of the system, however, is very different in this higher-pressure region. The halts, although more sluggish, are much more distinct, with the lengths increasing by as much as a factor of 10 over the values below the intersection. The lower of the two curves above 35 kbar is especially interesting in that the halt temperature decreases with increasing pressure up to about 55 kbar, where the halt temperature abruptly

starts increasing again. This behavior is similar to that found in elemental cesium.¹⁵

In determining melting points, we found it very difficult to obtain reliable values (even with rapid cooling and warming techniques) for samples in the composition range between the peritectic and eutectic, the break in the thermal curve for this region of composition being too gradual to obtain good values. For this reason, we have obtained only a partial phase diagram. Better melting points were obtained for the potassium-rich alloys. These data are recorded in Fig. 4. The maximum in the phase diagram suggests the formation of an NaK_2 intermetallic compound at high pressures. Since, however, we were never able to detect an additional invariant point (either eutectic or peritectic) in this region, the existence of NaK_2 is not confirmed. On the other hand, our failure to find the invariant point does not rule out its existence. A sluggish low-energy change can easily miss detection in a time-temperature study. An independent x-ray study at high pressures is planned to see if such a compound can be identified.

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