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SOLID-LIQUID PHASE EQUILIBRIA
IN THE SODIUM-POTASSIUM SYSTEM

by

J. Bevan Ott
Professor of Chemistry

and

J. Rex Goates
Professor of Chemistry

Brigham Young University
Provo, Utah

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Solid-Liquid Phase Equilibria in the Sodium-Potassium System

By J. B. Ott, J. R. Goates, D. R. Anderson
and H. T. Hall, Jr.
Department of Chemistry
Brigham Young University
Provo, Utah

Abstract

Thermal methods were used to determine with high precision, the solid-liquid phase equilibria diagram for the sodium-potassium system. The melting points of the pure metals and the solid solubility limits were better established by the use of ultra-pure elements and precision thermometry. Considerable effort was expended in a search for intermetallic compounds. No compounds other than Na_2K were formed.

Several investigators have made freezing point measurements on solutions of sodium and potassium in an attempt to determine the solid-liquid equilibrium phase diagram for this system.^{1,2,3,4,5,6} These early thermal investigations established the general boundaries of the phase diagram and identified a meritectically melting Na_2K compound. The measurements, made without the advantages of platinum-resistance-thermometry, high purity chemicals, and modern inert atmosphere facilities, were understandably lacking in detail and accuracy. More recent solid-liquid equilibria studies by MacDonald, et al.,⁷ using electrical resistance measurements, and by Rimai and Bloembergen,⁸ using nuclear magnetic resonance measurements, confirmed the earlier reported features of the phase diagram and identified the solid solution regions that had been suggested by Bornemann.⁶

The accuracy now possible from thermal methods is approximately an order of magnitude better than that reported by any of the previous studies. It was

the purpose of the present investigation to make use of improved thermal methods to obtain a detailed, accurate phase diagram of the Na-K system. We had particular interest in (1) establishing limits of solubility in the solid solution regions, and (2) thoroughly investigating the possibility of the existence of hitherto unreported intermetallic compounds.

EXPERIMENTAL

Chemicals

The freezing points of the pure metals were obtained with samples of very high purity sodium and potassium. The purification of these samples by fractional distillation has been described in the literature.⁹ Analysis of the sodium showed <10 ppm. potassium, while the potassium showed <10 ppm. sodium with smaller amounts of other impurities in each of the two metals.

Alloys with compositions in the regions where solid solutions form (<5 mole % solute) were made by adding successive increments of a 50 wt. % Na-K alloy to the samples of high purity Na and K. Alloy samples other than those mentioned above were made with MSA Research Corp. High Purity Grade potassium and J. T. Baker Reagent Grade sodium. The potassium was certified 99.97+ % pure by MSA. Labeled impurities in the sodium (other alkali metals were not listed) totaled 0.004 wt. %. Comparison of the melting point with the purified sample verified that the sodium was 99.9+ % pure.

Preparation of Samples

Preparation and handling of the alloy mixtures were carried out in a Vacuum/Atmospheres Corp. HE-133-5 "Vac Lab" using high purity argon gas for the inert atmosphere. Oxygen and water vapor concentrations were kept at levels of <1 ppm. by a Vacuum/Atmospheres Corp. HE-373B-1 purification train. Under these conditions, a Na-K liquid alloy (which seems to oxidize more rapidly

than the pure metals) would stay bright for several hours and would show only a slight oxide layer when left for several days.

Samples were prepared by weighing the sodium and potassium into a nickel crucible on a top-loading Mettler P160 pan balance which was accurate to $\pm$ 0.001 gm, and melting the material to form a liquid solution. The samples desired (generally about 20 gms.) were weighed into the freezing point apparatus by filling a syringe with the liquid alloy. The syringe and contents were weighed before and after injection into the sample tube.

Apparatus

Three types of time-temperature devices were used in making the measurements. Figure 1 shows the apparatus used for making most of the measurements. It is housed inside the glove box so that all operations from preparation of sample to measurements are made with minimal chance of contamination of the metals. The apparatus is suspended in the glove box from a brass plate at the top of the box. Temperatures are measured with a Leeds & Northrup platinum resistance thermometer which passes through the brass plate and into the thermometer well of the apparatus. A Veeco "Quick Vacuum Coupling" is used to seal the thermometer into the brass plate so that the thermometer can be readily raised and lowered into the well without contaminating the atmosphere in the dry box.

Rotary stirring is accomplished by driving the stainless steel stirrer (0-400 RPM) with a variable speed motor through a worm gear. Coolant (usually liquid nitrogen) circulated through the outer jacket and a heater tape wound around the outer jacket provide the temperature variability needed to obtain cooling and warming curves. The space between the jacket and the sample tube is connected to a vacuum/helium exchange gas system. The rate of cooling or warming is controlled by varying the pressure of the heat exchange gas in this space.

A second freezing point apparatus, which could be filled and sealed inside the glove box, and then removed from the glove box for the measurements was also used. The design of this apparatus is similar to that of an apparatus used in earlier work in this laboratory.¹⁰ Briefly, it consists of a 2.5 cm. O.D. by 21 cm. long pyrex tube sealed inside a 4 cm. O.D. x 22 cm. long tube, with the outer jacket thus formed connected to a high vacuum/exchange gas system. Temperatures are measured with a platinum resistance thermometer sitting in a well which goes down through the center of the freezing tube. Stirring is accomplished with a variable speed motor-driven stainless steel coil, which is sealed with soft elastic rubber tubing into the cap of the apparatus and moved vertically in the freezing tube. The vertical motion of the stirrer was not entirely satisfactory since it sometimes carried solid metal up the sides of the freezing tube out of contact with the liquid solution. For this reason, this apparatus was not suitable for obtaining accurate freezing points. However, the ease with which temperature cycling could be accomplished, simply by placing a bath around the lower part of the apparatus, made the apparatus very useful in exploratory investigations of invariant points.

The third apparatus used is in essence a cryogenic calorimeter. The calorimeter vessel is made of stainless steel, has a capacity of 75 ml. and is 3.5 cm. O.D. x 8.5 cm. long. A Leeds & Northrup low temperature (type 8164) platinum resistance thermometer is sealed in a tube along the axis of the cylindrical calorimeter, and a resistance heater is wound on the outside surface. A threaded plug is soldered shut on the end after the vessel is filled with alloy.

The sample vessel is suspended inside a massive aluminum cylindrical block, which is fitted with a heater and a thermocouple to provide temperature control of the surroundings of the sample. The block is then encased in a stainless steel jacket, which in turn is suspended in a five-foot long Dewar. The sample vessel and block are thermally insulated from the surroundings by evacuating the jacket

through a one-inch tube that extends out of the jacket and up through the top of the Dewar. The electrical leads from the sample vessel and block are also brought out through this opening.

A wide range of warming rates can be obtained by controlling the rate at which electrical energy is fed through the heater wire wound on the sample vessel. Because of the precise temperature control that is possible in this apparatus, it was used to very slowly thermally cycle and to anneal within narrow temperature ranges, making possible optimum conditions for compound formation and the establishment of equilibrium at a given temperature.

Temperature Scale

Temperatures were measured with Leeds & Northrup calibrated strain-free platinum resistance thermometers in combination with L & N high precision resistance recorders. The thermometers (#1705464 and #1720574) used to make the measurements inside the glove box and in the vertical stirring apparatus were calibrated by Leeds and Northrup at the ice, steam, sulphur, and oxygen points. The calibrations were 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, the values obtained agreed with the calibration to within 0.01°K . The thermometer (#1626895) used in conjunction with the calorimetric apparatus was calibrated by the National Bureau of Standards at sixteen temperatures over the range 10 to 400°K . We estimate our temperature scale to be accurate to within $\pm 0.02^{\circ}\text{K}$ over the range of the experimental measurements.

RESULTS AND DISCUSSION

Melting Points

The melting points of the Na-K solutions of varying compositions are given in Tables 1 and 2, and the complete phase diagram is shown in Figure 2. Except where otherwise noted, the data are judged to be accurate to within 0.1°K . A meritectic invariant point occurs at $280.07 \pm .05^{\circ}\text{K}$ and a composition of 0.402 mole fraction potassium. The eutectic is at $260.53 \pm .05^{\circ}\text{K}$ and 0.681 mole fraction potassium.

Our data differ significantly from the literature values that are summarized in the "Liquid Metals Handbook."¹ Our eutectic composition is shifted 1.5 mole per cent to the right (higher potassium) than the curve given in the handbook. As a result our values are as much as 3° higher than the handbook curve between the meritectic and eutectic compositions and 5° lower than the curve to the right of the eutectic. Agreement is somewhat better ($<1^{\circ}$) to the left of the meritectic composition. To the right of the meritectic composition, our data agree reasonably well with the warming data of van Bleiswijk.² Agreement is also fairly good with the data of MacDonald,⁷ especially in the potassium rich part of the curve. The melting point of Na (371.05°K) in this study agrees well with the value of Ginnings,¹² et al. (370.96°K) which was obtained in a calorimetric study of Na. Our melting point for pure K (336.86°K), however, is significantly higher than the calorimetric value (336.35°K) of Douglas, et al.¹³ The discrepancy can probably be explained by differences in purity of samples. Douglas et al. mentioned abnormally large increases in the melting point of their sample over part of the melting range. This they attributed to an uneven distribution of impurities in the liquid during the early stages of melting. We observed somewhat similar behavior in the melting curve of the ordinary research grade potassium (99.97+ % pure). The sample melted over a 1.1°K range with a stage of

relatively rapid temperature rise occurring as the sample passed through the 25 to 60 per cent melted region. The sample completed melting at a temperature near that of the uncorrected value reported by Douglas et al.¹³ The very high purity sample of potassium, on the other hand, melted uniformly over a temperature range of less than 0.15°K. Because of the formation of solid solutions the correction to zero per cent impurity used by Douglas et al.¹³ is not strictly valid in this system. For this reason, and because the melting points of both sodium and potassium are so sensitive to small amounts of impurities, very high purity sodium and potassium are a necessity if their melting points are to be obtained with high accuracy.

Solid Solutions

Liquidus and solidus points obtained in the regions of solid solution formation are listed in Table 2. For the most part, the solidus point could be read directly from the time-temperature curve by extrapolating the curves, before and after melting began, to an intersection point. On the steep portion of the diagram, however, the change in slope at the solidus point was too gradual to fix an intersection point with precision. To locate the solidus point under these circumstances, the data were re-plotted 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. With this region of the warming curve straightened, and with the added sensitivity of a difference plot included, the sensitivity of detection of the thermal changes occurring at the solidus point was greatly increased. The derivation of the equation follows:

Newton's Law of Cooling written in the simplest form is

$$\frac{\delta Q}{dt} = k (T_s - T) \quad (1)$$

where $\frac{\delta Q}{dt}$ is the time rate of transfer of heat, k is a constant, T_s is the temperature of the surroundings and T is the temperature of the system. At constant pressure, we can write

$$\frac{\delta Q}{dT} = C_p \quad (2)$$

where C_p is the heat capacity at constant pressure. Combining equations (1) and (2) to eliminate Q , and integrating (assuming C_p & T_s are constant) gives

$$\ln(T_s - T) = Kt + C \quad (3)$$

where C is the constant of integration and $K = -\frac{k}{C_p}$.

To evaluate T_s , three temperatures T_o , T_1 and T_2 are chosen from the time-temperature warming curve at times t_o , t_1 and t_2 respectively. Eliminating the constants in equation (3) gives

$$\frac{T_s - T_1}{T_s - T_o} = \left(\frac{T_s - T_2}{T_s - T_o} \right)^{\left(\frac{t_o - t_1}{t_o - t_2} \right)} \quad (4)$$

If one chooses the three points so that $t_o = 0$ and $t_2 = 2t_1$, (4) reduces to

$$\frac{T_s - T_1}{T_s - T_o} = \left(\frac{T_s - T_2}{T_s - T_o} \right)^{\frac{1}{2}} \quad (5)$$

which can be solved for T_s . Knowing T_s , one can evaluate the constants in

(3) from the relationships

$$C = \ln(T_s - T_o)$$

$$K = \frac{1}{t_1} \ln \left(\frac{T_s - T_1}{T_s - T_o} \right) \quad (6)$$

A difference plot $\Delta = \ln(T_s - T) - (Kt + C)$ versus t , is then made from the time-temperature data. According to equation (3), with no melting the plot

should follow along the abscissa. The point at which deviation from the abscissa begins, locates the solidus point. Figure 3 shows representative examples of plots made in this way for K in Na and Na in K.

The compositions of maximum solid solubility were obtained by varying the composition of the solutions until eutectic (or meritectic) first started to appear. The values of $0.008 \pm .001$ mole fraction K in Na and $0.046 \pm .003$ mole fraction Na in K agree well with the values obtained from extrapolation of the solidus lines. The solubility of Na in K is in excellent agreement with the value of 0.045 mole fraction Na determined by MacDonald, et al.⁷ from electrical resistivity measurements. However, our measurements show that the solubility of K in Na is appreciably lower than the value of 0.03 determined by MacDonald⁷ or the value of 0.025 estimated by Rimai and Bloembergen⁸ from NMR measurements.

It is interesting to note that regular solution theory predicts, as we found experimentally, that the solubility of Na in K is appreciably higher than that of K in Na. The same qualitative relationship is found by using the more extended calculations given by Speiser.¹⁴ Neither theoretical calculation gives quantitative agreement with the experimental data.

Solid Compound Investigation

The meritectic halt at 280.07°K , known to be associated with the solid compound Na_2K , was easily obtained and highly reproducible. A careful search for other possible intermetallic compounds was made, but with negative results.

A short and poorly defined temperature halt, suggestive of what one would observe from the sluggish formation of a small amount of another compound or a slow phase transition, was observed about $0.5 - 1$ degree above the eutectic temperature. Considerable effort was expended in an attempt to determine the cause of this halt. Measurements were made in the vertical-mixing apparatus

outside the glove box where rapid temperature cycling was possible, in the rotational-mixing apparatus inside the glove box where mixing was possible with less chance of air contamination and oxide formation, and inside the sealed calorimetric apparatus where no stirring or contamination were possible, but where very slow cooling and warming and long periods of annealing were easily obtained. The results of these measurements may be summarized as follows:

- (1) The halt exists on both sides of the eutectic and at the eutectic composition. There are no consistent changes in the length of the halt with composition of the solution.
- (2) After annealing the sample in the sealed container just above the eutectic temperature for a number of days, the halt disappears. Annealing in the vertical stirring apparatus (where oxide formation was evident, probably due to air diffusion through the rubber parts) under the same conditions produced fairly long halts. The rotational stirring apparatus produced shorter and erratic halts.
- (3) The eutectic halt is stable. No amount of annealing changed the amount of eutectic formed.

These observations rule out the possibility that the halt is due to the formation of another intermetallic compound, or that the halt represents any other stable feature of the Na-K diagram.

The second observation suggests that an irreversible oxide reaction may be responsible for the halt, since the halt disappeared with annealing in the sealed apparatus where no new oxide could form.

It is also possible that the method of cooling and warming a sample could account for these anomalous and transitory results. MacDonald⁷, for instance, found that the resistivity on solidifying Na-K alloys did not always recover to the original value. This he attributed to cavity formation.

Considerable effort was made to form intermetallic compounds other than Na_2K . Samples with compositions corresponding to NaK and NaK_2 were cycled slowly and held for several days at various temperatures in the calorimetric apparatus in an attempt to induce solid compound formation. No evidence of such formation could be detected. Cycling in the vertical-stirring apparatus of a number of samples covering the composition range 0.4 to 0.9 mole fraction K also produced negative results. We conclude that Na_2K is the only solid compound formed at atmospheric pressure in the Na-K system.

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Table 1

Melting Points

Sodium-Potassium System

<u>Mole Fraction K</u>	<u>T, °K</u>	<u>Mole Fraction K</u>	<u>T, °K</u>	<u>Mole Fraction K</u>	<u>T, °K</u>
0.0000	371.05	.4900	277.11	.6753	261.20
.0120	366.64	.4994	276.56	.6806	260.53
.0530	352.61	.4997	276.51	(.6807) ^b	260.53 ^b
.0998	339.00	.5198	275.57	.6849	261.31
.1572	324.95	.5209	274.85	.6950	263.42
.2002	315.65	.5380	274.24	.7000	264.60
.2351	309.09	.5483	273.50	.7048	265.57
.2666	303.19	.5484	273.56	.7352	271.32
.2833	300.30	.5672	272.20	.7716	279.01
.3048	296.75	.5940	269.95	.8020	285.93
.3302	292.43	.5967	269.62	.8253	291.35
.3574	288.04	.6077	268.55	.8499	297.30
.3715	285.51	.6309	266.31	.8675	301.80
.3858	283.12	.6499	264.28	.9107	312.52
.4008	280.09	.6535	263.76	.9500	323.40
(.4020) ^a	280.06 ^a	.6603	262.95	1.0000	336.86
.4495	278.76	.6680	262.05		
.4688	277.97	.6720	261.45		

a- meritectic point

b- eutectic point

Table 2

Freezing Points

Solid Solubility Region

<u>Mole Fraction Potassium</u>	<u>Liquidus K°</u>	<u>Solidus K°</u>	<u>Mole Fraction Potassium</u>	<u>Liquidus K°</u>	<u>Solidus K°</u>
<u>Potassium in Sodium</u>					
.0000	371.05	-	.0073	368.31	329.0 ^a
.0012	370.52	367.25	.0083	367.92	Meritectic
.0020	370.21	364.98	.0099	367.25	Meritectic
.0050	369.09	355.0 ^a	.0120	366.64	Meritectic
.0064	368.59	344.8 ^a			
<u>Sodium in Potassium</u>					
1.0000	336.86	-	.9600	325.60	289.6 ^a
.9983	336.28	334.88	.9568	325.06	283.4 ^a
.9965	335.69	333.19	.9519	324.09	Eutectic
.9944	335.33	331.31	.9500	323.40	Eutectic
.9898	334.03	326.80	.9410	321.11	Eutectic
.9790	331.07	315.50	.9300	317.94	Eutectic
.9689	328.27	303.71			

a- less accurate values on the steep portion of curve

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Fig. 1 Freezing Point Apparatus

Fig. 2. Solid-liquid phase diagram for the sodium-potassium system

Fig. 3 Representative graphs for determining the solidus point in the solid solution region of the phase diagram