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SOLID-LIQUID PHASE EQUILIBRIA
IN THE SODIUM-RUBIDIUM ALLOY SYSTEM

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Solid-Liquid Phase Equilibria
in the Sodium-Rubidium Alloy System

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Abstract

Thermal methods were used to determine with high precision, the solid-liquid phase equilibria diagram for the sodium-rubidium system. The results differ greatly from those of earlier workers, especially near the eutectic composition where differences in melting points as large as 25° K occur. A detailed search was made for possible intermetallic compounds (especially Na₂Rb). Neither slow temperature cycling in the temperature range where compound formation could occur nor extended periods of annealing just above the eutectic temperature produced any evidence for compound formation. A 2:1 (sodium to rubidium) sample was subjected to 60,000 atmospheres pressure. Again, no evidence was obtained for solid compound formation.

Freezing point measurements have been made by several workers^{1,2,3} on solutions of sodium and rubidium in an attempt to determine the solid-liquid phase diagram for this system. The measurements were made a number of years ago without the advantage of high purity metals, platinum resistance thermometry, and modern inert atmosphere facilities. As a result, the data are in very poor agreement, especially on the rubidium-rich side of the eutectic,

where very few data points were obtained. Comparison of the data available indicated differences in temperature of as much as 15° between the data of Rinck¹ and that of Gorla². No evidence was found in any of the previous work for intermetallic compound formation. This seemed somewhat surprising since a meritectically melting Na_2K intermetallic compound had been well established in the sodium-potassium system,^{4,5} and a sluggishly forming meritectically melting Na_2Cs compound had been reported in the sodium-cesium system.^{6,7}

As a part of our investigation of alkali metal mixtures, we sought to obtain a detailed and accurate solid-liquid phase diagram for this system. Of special interest was the possibility for the formation of intermetallic compounds such as Na_2Rb .

EXPERIMENTAL

Chemicals

High purity (99.8% minimum) rubidium was obtained from the Kawecki Chemical Company. Batch analysis of the material by Kawecki Chemical indicated .034 mole % Cs, .017 mole % K, .018 mole % Na, .015 mole % Si with negligible amounts of other impurities. Oxygen analysis was not available. However, calculations from the change in melting point with fraction melted indicated less than 0.02 mole % oxygen. The rubidium is considered to be better than 99.9% pure.

"Reactor Grade" sodium was obtained from the U. S. Industrial Chemical Company. Specifications for "Reactor Grade" sodium limit the impurities to <200 ppm K, <100 ppm oxygen, <50 ppm Rb and smaller amounts of other impurities. Comparison of the melting point of this sodium with our measurements of an ultra-pure sample as described in the literature⁵ limits the impurities to <0.05 mole % total.

Sample Preparation

Preparation and handling of the alloy mixtures were carried out in a Vacuum Atmospheres Corporation 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 sodium and rubidium 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 liquid solution, which was then transferred into the freezing point apparatus. To conserve rubidium metal, some samples were prepared in a similar manner by dilution of an alloy sample of known composition with sodium or rubidium.

Apparatus

The general design of the apparatus for making the freezing point measurements has been described in the literature.⁵ Briefly, the sample is contained in a double-jacketed stainless steel sample tube. Coolant (usually liquid nitrogen) circulating 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 inner jacket is connected to a vacuum/helium exchange gas system. The rate of cooling or warming can be controlled by varying the pressure of the heat 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. Temperatures are 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 and into a thermometer well in the center of the sample tube. It was calibrated by Leeds and Northrup Co., 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, the values obtained agreed with the calibration to within 0.01°K . We estimate our temperature scale to be accurate to at least $\pm 0.02^{\circ}\text{K}$ over the range of the experimental measurements.

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.

RESULTS

Freezing Point Measurements

Freezing points were determined over the entire composition range from time-temperature cooling and warming curves. "Clumping" of the soft solid metal as it was formed, made the melting points less reliable than the freezing points. The results are summarized in Table I and Figure 1. The values are considered accurate to $\pm 0.15^{\circ}\text{K}$ except for the five points on the steep portion of the curve immediately on the sodium-rich side of the eutectic. Here the uncertainty may be as high as $\pm 0.5^{\circ}$. The time-temperature cooling and warming curves in this region gave only a small break at the melting point.

The eutectic point occurs at $268.65 \pm 0.05^{\circ}\text{K}$ and 0.821 mole fraction rubidium. From 0.0–0.4 mole fraction rubidium, the data are in reasonable agreement with the earlier data of Rinck¹ and of Gorla.² However, between 0.4 mole fraction rubidium and the eutectic composition, the data of references

(1) and (2) differ greatly from our values. The difference becomes largest around 0.7 mole fraction rubidium where the data of Rinck¹ and Gorja² are 17 and 25 degrees lower, respectively. As mentioned earlier, even with the advantages of high precision resistance thermometry used in this study, it was difficult to determine melting points in this region. Apparently both Rinck and Gorja were observing something other than the melting point. Both of these workers obtained a eutectic composition approximately 7 mole % lower than the value obtained in this study. The discrepancy is due to the large difference in the freezing point data on the sodium-rich side of the eutectic as discussed above. On the rubidium-rich side of the eutectic, our data are in good agreement with the two measurements made in this region by Rinck.¹ However, the one data point obtained in this region by Gorja², and generally considered as representative of the freezing curve in this region⁸, is 18° high.

The eutectic halt was detectable in all samples we made measurements on from .005 to .989 mole fraction Rb and uncertain beyond these points. Cycling and annealing the samples at the limiting compositions caused no decrease in the length of the eutectic halt, indicating that equilibrium conditions were attained. Disappearance of the eutectic halt below mole fraction Rb of 0.005 and above 0.989 could either indicate the beginning of solid solution regions, or it could simply mean that we had exceeded the limit of detection of the small amount of eutectic available to form at these compositions. Unfortunately, the steepness of the phase diagram in these narrow composition regions rules out the feasibility of detecting solidus points on the cooling curves. The one conclusion that can be made is that solid solubility in these systems is very low, with 0.005 mole fraction Rb in Na and 0.011 mole fraction Na in Rb representing upper limits for the solubility.

Low solid solubilities in this system are predictable by theoretical

methods. Both from consideration of size factor and regular solution theory, these solubilities would be expected to be lower than the analogous ones in the Na-K system, in which solubilities of less than 0.008 mole fraction K in Na, and less than 0.046 mole fraction Na in K were established.⁵ The present Na-Rb results, however, disagree with the findings of Rimai and Bloembergen⁹, who, using nuclear magnetic resonance, reported the solid solubility of Rb in Na to be several times larger than the limit given above. They did not measure the extent of solubility of Na in Rb, which would be expected to be larger than the reverse.

Search for Intermetallic Compounds

Considerable effort was expended in an attempt to form an intermetallic compound, especially Na_2Rb (analogous to Na_2K and Na_2Cs). Solutions with compositions corresponding to Na_2Rb , NaRb , and NaRb_2 were cycled repeatedly in the freezing point apparatus in the temperature range from the eutectic to the melting point. Neither slow cooling, slow warming, or annealing at the eutectic followed by slow warming produced any halts in this temperature region indicative of compound formation. Occasionally, during the warming periods, a change in slope in the warming curve was observed about one degree above the eutectic point. Similar behavior was observed in the sodium-potassium system.⁵ It was shown in that system that the inflection did not result from the formation of a stable compound.

To check the possibility that Na_2Rb may form in this system by a very sluggish reaction, a sodium-rubidium alloy (mole fraction Rb = 0.333) was put in an apparatus where very slow cooling, warming, and annealing were easily obtained. This apparatus has been described previously in the literature.⁵ It is essentially a cryogenic calorimeter. The sample (~75 ml.) is sealed inside a stainless steel container which is surrounded by a massive heat shield. The combination is enclosed by an evacuated container. This outer container

sits inside a stainless steel Dewar flask, which can be filled with coolant and held at low temperatures. The cylindrical sample container has a resistance heater wound on its outer surface. When in operation, the heat shield is usually kept colder than the sample container and the small heat leak to the heat shield is used to obtain very slow cooling curves. By compensating with electrical heating, the sample may be held at any temperature or warmed at any desired rate. With this apparatus it is easily possible to anneal the sample over a very narrow temperature range for hours, or even for days. Temperatures were measured with a Leeds and Northrup low temperature (type 8164) platinum resistance thermometer in combination with a Leeds and Northrup high precision resistance recorder. This thermometer (#1626895) was calibrated by the National Bureau of Standards at sixteen temperatures over the range 10 to 400° K.

A number of experiments carried out in this apparatus in an attempt to form Na_2Rb indicate that if an intermetallic compound forms in this system, it would have to do so at a very slow rate. The experiments included (1) alternate slow cooling and slow warming of the sample over periods of 12-24 hours in a temperature range from above the melting point to well below the eutectic, and (2) annealing this sample for long periods of time. The annealing procedure consisted of holding the temperature of the sample within ^a one degree range immediately above the eutectic temperature for periods of 6-8 hours, then slowly cooling down through the eutectic over a period of 12 hours, and finally warming through the eutectic. The procedure was repeated five times over a six day period, during which time the temperature of the sample was never allowed to rise more than one degree above the eutectic temperature. Significantly, the length of the eutectic halt, measured during the warming part of the five cycles at a constant rate of input of energy, remained constant, indicating no evidence that a slow conversion to compound could be taking place. At the

conclusion of the six day period, the sample was warmed past its melting point. No temperature halts, indicative of compound formation were obtained in either (1) or (2). However, the change in slope as discussed previously was still observed.

In a further attempt to form an intermetallic compound, an alloy (0.328 mole fraction rubidium) was studied at high pressures. The sample was encapsulated in polyethylene, placed in a graphite cylinder and subjected to pressures up to 60,000 atmospheres in one of the tetrahedral presses available in the high pressure laboratory at Brigham Young University. The design of the high pressure apparatus has been well described in the literature.^{10,11}

Time-temperature heating and cooling curves were obtained on the sample at various pressures by using the graphite capsule as a resistance heater. Temperatures were measured with a chromel-alumel thermocouple. A halt in the cooling or warming curve due to the eutectic was easily identified. The eutectic increased from 269°K at atmospheric pressure to 397°K at 60,000 atmospheres. No other halts were observed at any pressure. Comparable measurements in the sodium-potassium system gave both a eutectic halt and a meritectic halt over the same pressure range.¹² It is concluded that pressure does not bring about the formation of an Na_2Rb intermetallic compound.

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Table 1

Freezing Points

Sodium-Rubidium System

<u>Mole Fraction Rb</u>	<u>T, °K</u>	<u>Mole Fraction Rb</u>	<u>T, °K</u>
.0000	371.05	.6187	313.51
.0050	369.37	.6786	304.3 ^a
.0099	367.34	.7303	293.3 ^a
.0394	358.18	.7345	292.0 ^a
.0613	351.78	.7788	280.2 ^a
.0780	348.91	.8137	270.7 ^a
.1067	344.62	(.8210) ^b	268.65 ^b
.1774	338.57	.8385	271.77
.2001	337.59	.8584	275.59
.2634	334.94	.8606	275.95
.3005	333.61	.8863	281.56
.3454	331.91	.9021	285.04
.3565	331.74	.9283	291.49
.4246	328.86	.9584	299.99
.4585	327.45	.9889	309.51
.4956	325.07	.9937 ^c	310.73
.5556	320.28	1.0000	312.45

^a--less accurate values on steep portion of the curve.

^b--eutectic point.

^c--no eutectic observed in this sample.

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Fig. 1 Solid-Liquid phase diagram for the sodium-rubidium system