3 exp

Technical Progress Report
to the United States Atomic Energy Commission
on Contract No. AT(11-1)-1707

Report No. C00-1707-11

Contract Period: May 1, 1967 to Aug. 31, 1971

THIS DOCUMENT CONFIRMED AS
UNCLASSIFIED
DIVISION OF CLASSIFICATION
BY QH Kahn / amh
DATE 9/28/71

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

by
J. Bevan Ott
Professor of Chemistry

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

and
J. Rex Goates
Professor of Chemistry

Brigham Young University
Provo, Utah

August 31, 1971

R1528

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

fy

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

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

By J. Bevan Ott, J. Rex Goates, and Chen C. Hsu

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

Thermal methods were used to determine solid-liquid phase equilibria points for the ternary sodium-potassium-rubidium alloy system. Two temperature halts were observed for most of the compositions. The low temperature halt is a eutectic with a minimum value near 255.3°K .

During the past several years we have determined the solid liquid phase diagrams for all the binary mixtures of the alkali metals Na, K, Rb, and Cs¹⁻⁵. We found an incongruently melting Na_2K compound in the sodium-potassium system. Sodium and rubidium form a simple eutectic system² while potassium and rubidium form a continuous solid solution with a freezing point minimum.⁵ Tepper, King, and Greer⁶ have investigated the ternary system Na-K-Cs. They found a ternary eutectic at 194°K . It is interesting that this eutectic is so much lower in temperature than the binary eutectic of the Na-K system at 260.53°K (the lowest solid-liquid equilibrium point in any of the binary systems).

Little information is available on the Na-K-Rb system. In view of the behavior of the Na-K-Cs ternary, an investigation of the ternary invariant points of the Na-K-Rb system appeared worthwhile.

EXPERIMENTAL

Chemicals. 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 literature¹ limits the impurities to < 0.05 mol % total.

High-purity grade potassium certified as 99.97% pure was obtained from MSA Research Corp. High-purity (99.8% minimum) rubidium was obtained from the Kawecki Chemical Company. Batch analysis of the material by Kawecki Chemical indicated 0.034 mol % Cs, 0.017 mol % K, 0.018 mol % Na, 0.015 mol % 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 mol % oxygen. The rubidium is considered to be better than 99.9% pure.

Sample Preparation. The alloy mixtures were prepared and manipulated in a Vacuum Atmospheres Corp. argon glove box. Oxygen and water vapor concentrations in the box are < 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 potassium and cesium inside the glove box on a top-loading Mettler P-160 single-pan balance (± 0.001 gram accuracy). The samples were weighed into a nickel crucible, melted to form a homogeneous mixture, and then transferred into the freezing-point apparatus.

Apparatus and Temperature Scale. The stainless steel, rotary-stirring, vacuum-jacketed freezing point apparatus is described in the literature.² This apparatus is suspended inside the 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.

Temperatures were measured with a Leeds and Northrup platinum resistance thermometer in combination with a Leeds and Northrup high-precision resistance recorder. The thermometer was calibrated by Leeds and Northrup at the ice, steam, sulfur, and oxygen points. We checked the calibration during the measurements at the ice point (273.150°K), the mercury freezing point (234.29°K), and the sodium sulfate decahydrate transition temperature (305.534°K). The values obtained agreed with the calibration to within $\pm 0.01^{\circ}\text{K}$. We estimate our temperature scale to be accurate to at least $\pm 0.02^{\circ}\text{K}$ over the range of the experimental measurements.

Experimental Procedure. A binary mixture of two of the metals was prepared whose mole ratio was as close to 1:1 as possible. Varying amounts of the third metal were added to the 1:1 binary mixture and time-temperature cooling and warming curves were obtained. This procedure was followed for all three of the combinations of the metals. In this manner, the effect of the third component on each of the binary systems could be determined.

RESULTS

A freezing point and a low temperature halt were obtained for all samples. A high temperature halt was also obtained for most of the compositions. The results are given in Table I. All values are considered accurate to at least $\pm 0.15^{\circ}\text{K}$. The low temperature halt is considered to be a ternary eutectic;

the sample froze completely during this halt. The high temperature invariant point was not observed in the samples with the 1:1 sodium-rubidium ratio. In each of these samples, a change in the slope of the time-temperature curve was observed at 268.25°K .

The effect of each of the components on the low temperature halt is shown in Fig. 1. The curves where either potassium or rubidium were varied both go through a minimum at 255.3°K , a value that is only 5°K lower than the Na-K binary eutectic point.

The authors gratefully acknowledge the support given this project by the United States Atomic Energy Commission under contract No. AT (11-1)-1707.

Table 1

Thermal Data for the Sodium-Potassium-Rubidium System

Composition; Mol %			Approximate Mole Ratio Na:K:Rb	Freezing Point °K	Low Temperature Halt °K	High Temperature Halt °K
Na	K	Rb				
33.43	33.23	33.34	1:1:1	282.06	255.74	270.22
40.16	39.78	20.06	1:1:1/2	283.88	255.36	273.00
25.18	24.95	49.87	1:1:2	283.18	257.68	271.67
20.49	20.29	59.22	1:1:3	303.93	258.97	271.17
38.37	23.37	38.26	1:5/3:1	284.27	257.19	----
30.15	39.82	30.03	1:3/2:1	265.81	255.35	----
24.36	51.37	24.27	1:2:1	272.24	255.52	----
20.01	60.05	19.94	1:3:1	283.56	256.15	----
20.11	39.76	40.13	1:2:2	273.39	255.62	268.25
49.91	24.94	25.15	1:1/2:1/2	293.35	256.36	271.72
59.92	19.95	20.13	1:1/3:1/3	305.17	257.45	271.83
73.04	16.96	10.00	----	314.36	255.13	274.69
59.98	29.86	10.16	----	292.90	255.26	276.60

Fig. 1. Low temperature halts, sodium-potassium-rubidium system

LITERATURE CITED

1. Ott, J. B., Goates, J. R., Anderson, D. R., and Hall, H. T. Jr., Trans. Faraday Soc., 65, 2870 (1969).
2. Goates, J. R., Ott, J. B., and Hsu, C. C., Trans. Faraday Soc., 66, 25 (1970).
3. Ott, J. B., Goates, J. R., and Oyler, D. E., Trans. Faraday Soc., 67, 31 (1971).
4. Goates, J. R., Ott, J. B., and Hall, H. T. Jr., J. Chem. Eng. Data, 16, 83 (1971).
5. Goates, J. R., Ott, J. B., and Delawarde, E., Trans. Faraday Soc., 67, 1612 (1971).
6. Tepper, F., King, J., and Greer, J., "The Alkali Metals", Special Publication No. 22, The Chemical Society, Burlington House, London, 1967, pp 23-31.