ACKNOWLEDGMENT

This work was conducted with the support of the U. S. Atomic Energy Commission through the Inorganic Materials Research Division of the Lawrence Radiation Laboratory. The authors wish to thank Ralph Hultgren, K. K. Kelley, and Leo Brewer for helpful discussions, and Victor Zackay for providing the sample.

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RECEIVED for review January 17, 1964. Accepted May 8, 1964.

Phase Equilibria in the Potassium Hydroxide–Sodium Hydroxide System

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Equilibria in the potassium hydroxide–sodium hydroxide system have been investigated through observation of cooling curves. A eutectic point at 170° and 41 wt.% sodium hydroxide was found. Solid-solid transition temperatures for both components are lowered by the presence of the other. Solubility of NaOH up to about 10% in solid KOH and much smaller solubility of KOH in solid NaOH is indicated.

THE KOH-NaOH system has been investigated incidental to a project involving the use of the alkali hydroxides as solvents. The results are not in agreement with the phase diagram presented by Hevesy in 1910 (*2*). A more recent study by Reshetnikov and Unzhakov, as far as can be judged from a brief abstract (*3*), appears to agree with our findings but, in view of the inaccessibility of the Russian publication in which this work appears, it was thought desirable to present our phase diagram as deduced from cooling curves for various mixtures of the two components.

EXPERIMENTAL

The reagent grade potassium hydroxide employed was found by analysis to contain 14.8% water and 0.6% potassium carbonate while the sodium hydroxide initially was 0.6% water and 0.3% sodium carbonate. The potassium hydroxide was heated and held at 475–500° for 24 hours in a nickel container to remove water and the sodium hydroxide in an aluminum container was kept at 400° for 4–6 hours. The hydroxides as used contained 0.3 to 0.7% carbonate. It is estimated that the observed freezing points are 0.5 to 1.2° below what they would have been in the absence of carbonate. Although the fused samples were not completely protected from the atmosphere by dry nitrogen, molten samples could be kept for several days without absorbing enough water or carbon dioxide to cause a detectable change in their freezing points.

Aluminum cylinders holding about 50 grams total hydroxide were used for the cooling curve measurements. These cylinders were placed in an electric furnace to melt the hydroxides and regulate the rate of cooling. Cooling rates of about 1-2 deg./min. were used to ensure equilibrium conditions; no appreciable supercooling was observed. The tendency to creep up the walls is much less with aluminum than with nickel and the uncertainty of composition due to creep is minimized by its use. Nickel was required for the dehydration of the potassium hydroxide because its initially higher water content enables it to attack aluminum. When thoroughly dehydrated, however, no significant attack on aluminum is observed at temperatures lower than 450°.

Temperatures were measured by a chromel-alumel thermocouple which was calibrated with samples of tin, lead, and zinc whose freezing points had been certified by the National Bureau of Standards. Thermocouple EMF's were measured with a Leeds and Northrup type K-2 potentiometer and type E galvanometer. The thermocouple hot junction was immersed in the melt without protection, since there were no observable differences in the calibrated freezing points whether a protection tube was used or not.

RESULTS

Table I presents, for the various mixtures used, the temperatures at which breaks were observed in the cooling curves, interpreted as initial freezing, eutectic, and transition temperatures. These temperature-composition values are shown as points connected by the continuous lines in Figure 1. The dashed lines on the potassium hydroxide side refer to hypothetical equilibria involving solid solution and were not determined experimentally. A eutectic at 170° and 41% is clearly indicated, in contrast to the phase diagram of Hevesy (*2*) which shows continuous solid

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Table I. Freezing Points of NaOH-KOH Mixtures

Wt. of NaOH	F.P., ° C.	Eutectic, ° C.	Trans., ° C.
0.0	409.5	...	247.0
3.7	390.8	171.5	234.2
7.3	368.2	166.5	227.0
10.9	348.5	...	222.8
13.8	328.0	168.8	223.5
19.0	296.2	...	219.2
22.4	272.8	...	215.5
26.1	230.5	169.8	219.2
31.2	207.8	170.0	...
35.4	180.5	169.5	...
38.3	...	169.8	...
43.1	174.5	168.8	...
46.1	186.2	168.2	...
52.9	202.0	170.0	...
57.8	217.0	170.5	...
72.0	252.2	170.8	...
81.1	273.2	170.0	...
83.2	275.8	170.2	...
90.8	291.5[a]	169.8	...
93.2	298.0	169.5	293.0
100.0	319.8	...	294.6

[a] The freezing point and transition point are apparently superimposed as only one halt in the cooling curve was found.

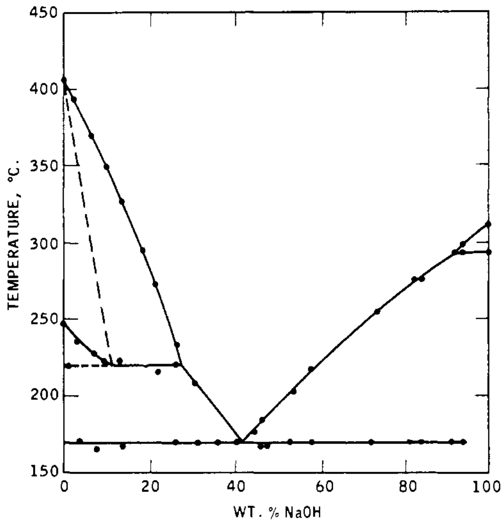

Figure 1. Solid-liquid equilibrium in the KOH-NaOH system

solutions with a minimum in the liquidus curve. The formation of solid solution on the potassium side has been inferred from the fact that the solid-solid transition, initially at 247°, is lowered as much as 28° on the addition of sodium hydroxide. That the sodium hydroxide content of the solid solution is limited is evidenced by the fact that the transition temperature becomes substantially constant when the sodium hydroxide content of the system reaches about 10%. If the possibility of solid solution formation is disregarded, a heat of fusion of 2200 cal. per mole may be calculated for potassium hydroxide from the freezing point lowering. A similar calculation from freezing point lowerings produced by potassium carbonate yields a value of 1870 cal. per mole. With potassium carbonate as solute the transition temperature is lowered by a maximum of only 6°. Presumably there is some, but less, solid solution formed in the $KOH-K_2CO_3$ system. Hence the value of 1870 is still too high but should be nearer to the correct heat of fusion. No calorimetric measurement of the heat of fusion could be found in the literature to check this point. Since the eutectic halt was found with only 3.7% sodium hydroxide, the extent to which NaOH may be incorporated as a solid solution in the low temperature form of KOH must be very small. On the sodium hydroxide side of the diagram the solubility of KOH in solid NaOH appears to be smaller since the transition temperature is lowered but 2–3°. Furthermore, a heat of fusion of 1560 cal. per mole as calculated from the lowering of the sodium hydroxide freezing point is in reasonable agreement with the calorimetric value of 1520 calories (*1*).

ACKNOWLEDGMENT

The authors wish to acknowledge support by the U. S. Atomic Energy Commission under Contract AT(30–1)–1881.

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Received for review February 22, 1964. Accepted June 15, 1964.

Refractive Index of Phosphoric Acid Solutions at 25° C.

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ONLY A FEW measurements of refractive indexes of phosphoric acid solutions have been reported (*2*, *3*) since Wagner (*10*) in 1907 published results for solutions in the range 0 to 4*M* at 17.5° C. None of the results are widely useful because each set covers only a short concentration range and was made at a different temperature and with a different spectral source line.

In a study by the Gouy method of the diffusion of phosphoric acid solutions (*4*), data were obtained on the refractive increment over the concentration range 0.04 to 16*M* (0.4 to 90% H_3PO_4). From these data were obtained refractive indexes at 25° C. and 5460.7 A. of aqueous phosphoric acid solutions over the concentration range covered.

The Gouy apparatus was slightly modified (*4*) from that of Gosting and coworkers (*7*). When the instrument is used to determine diffusion coefficients, the boundary between the two interdiffusing solutions is formed in a collimated beam of monochromatic light. The gradient of refractive