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Henry's Law Constant for Water in the Eutectic Molten Salt System NaOH-KOH

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Henry's law constants for water in the molten eutectic system NaOH-KOH have been measured by a gravimetric technique at different temperatures between 250 (523 K) and 450 °C (723 K). The results fit the equation $\ln k = -(8081)/T + 10.8$ (where T is the temperature in Kelvin and k is Henry's constant in atm mol^{-1} kg). These results are compared with published data for pure NaOH.

Introduction

The Henry's law constant for water in pure NaOH as a molten salt has been measured both by Rahmel and Kruger (*1*) and by Hoyt (*2*). The former authors found that the value of the constant was $10^{4.88-(3210/T)}$ atm mol^{-1} kg (equal to $\ln k = -7391/T + 11.2$) while the latter found values of 0.63 and 1.20 for the constant at temperatures of 640 and 690 K, respectively. Both determinations relied on the measurement of the amount of water dissolved in the melt as a function of the vapor pressure of water in the gas phase. This work has been reviewed elsewhere (*3*).

In the course of investigations by us it was found necessary to know the mole fraction of water in a melt consisting of 63.1 mol % NaOH and 36.9 mol % KOH—a eutectic composition having a melting temperature of 185 °C (*4*). This information does not appear in the literature.

The results reviewed above were obtained by voltammetric (*1*) and gravimetric (*2*) techniques. As a thermobalance was available, it was concluded that the latter technique would prove the more convenient. Hoyt (*2*) used the technique of allowing a melt to come to equilibrium with nitrogen saturated with water vapor, before finding the increase in weight compared with the dry melt, by external weighing. It was felt that the determination might prove to be more accurate if the procedure was adapted for a thermobalance where the weight may be found internally while the melt was still under a nitrogen atmosphere.

Experimental Section

AnalaR-grade NaOH and KOH were weighed out and mixed in the correct proportions to make the eutectic composition in nickel crucibles which had been previously heated in an oxidizing atmosphere to 700 °C in order to form an oxide film impervious to molten hydroxides. The sample weights varied between 1 and 2 g for each determination.

Dry nitrogen was obtained by passing cylinder nitrogen through a purification train consisting of one column of NaOH pellets (to remove CO_2) followed by a second containing Union Carbide "Type 4A" molecular sieve and self-indicating silica gel to remove H_2O. All experimental procedures except for the simple manipulations were carried out under an atmosphere of nitrogen purified in this train. Nitrogen purified in this way caused no weight gain (to within 0.1 mg in 8 h) to a sample of dry NaOH pellets (~1 g) at room temperature in the apparatus. Care was taken to ensure that the purge rates were high enough to preclude the back-diffusion of CO_2 into the melt via the furnace tube which is, of necessity, open at the bottom. Failure to ensure this led to a steady weight gain due to the pickup of CO_2. As this was detectable, any runs subject to this error were discounted.

Table I. Henry's Law Constant for NaOH-KOH at Different Temperatures

	k, atm mol^{-1} kg				
temp, K	run 1	run 2	run 3	av k	SD
723	0.60	0.89	0.50	0.66	0.20
673	0.30	0.45	0.30	0.35	0.09
623	0.09	0.15	0.11	0.12	0.03
573	0.027	0.030	0.029	0.029	0.002
523	0.0086	0.0110	0.0090	0.0095	0.001

A Stanton-Redcroft recording thermobalance was used for the weight determinations, the balance being sensitive to changes of 0.1 mg or more. The furnace and arrangements to provide nitrogen saturated with a known amount of water are shown in Figure 1. The nitrogen either was available dry and CO_2 free straight from the purification train or was saturated with water at a controlled temperature. This latter effect was achieved by first bubbling the nitrogen through a vessel containing water at 70 °C via a glass sinter (porous sintered glass frit). This gas stream was then passed through two water-filled Dreschel bottles, fitted with both sinters (porous sintered glass frits) and ballotini (spherical glass beads of diameter ~0.5 cm) and kept at a thermostatically controlled temperature in a water bath capable of holding a set temperature to ±0.1 °C over several hours. The temperature of the bath was controlled as close as possible to room temperature to minimize any change in the vapor pressure of the water after the gas stream had left the system. The actual vapor pressure of the water in the gas was found by using standard tables (*5*).

The furnace temperature of the thermobalance was controlled by a Pye Ether controller, the measured temperature control being within ±5% when a constant temperature was held for more than ~10 min.

An experimental run was carried out by first heating the crucible and melt to 450 °C under dry nitrogen until the trace on the thermobalance showed a constant weight, indicating that the melt was completely dry. The nitrogen supply was then passed through the saturation system described above and the crucible allowed to come to a new equilibrium weight. The weight difference between the two equilibrium points on the trace was taken to be the amount of water dissolved in the melt at this temperature. The temperature was then allowed to fall to a new temperature with the crucible still under the "wet" nitrogen. The new equilibrium position was then taken to be representative of the extra water dissolved at this lower temperature (in excess of that dissolved at the higher temperature).

This was repeated at lower temperatures down to 250 °C. The entire run was performed 3 times.

Results and Discussion

A typical curve taken from the thermobalance is shown in Figure 2. The results calculated from Henry's constant (k) are presented in Table I. These are calculated from the weights

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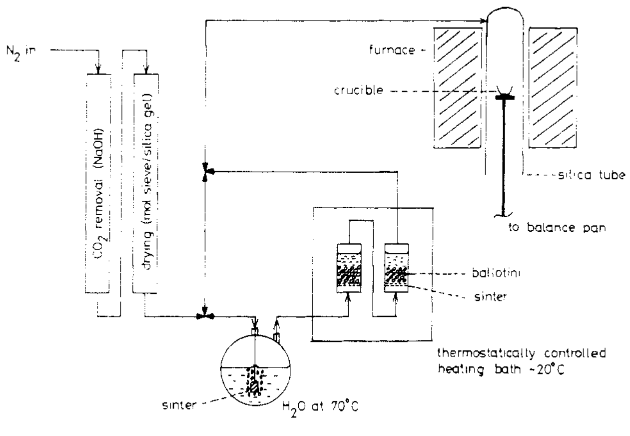

Figure 1. Nitrogen purification/saturation apparatus.

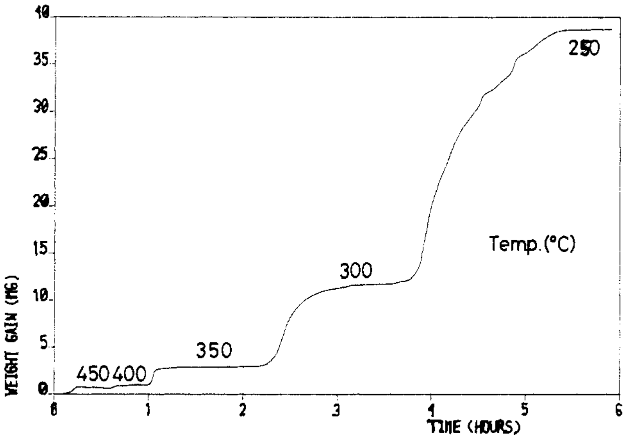

Figure 2. Typical TG curve.

obtained from the experimental traces; the partial pressure of water in the nitrogen (the saturated vapor at room temperature in the thermostatically controlled bath) was found from tables (*5*).

Using Henry's law

$$P_{H_2O} = kN_{H_2O}$$

where P_{H_2O} = partial pressure of H_2O in nitrogen, N_{H_2O} = amount of H_2O dissolved in melt (in mol kg^{-1}), and k = Henry's constant (in atm mol^{-1} kg).

The results in Table I are plotted as ln k against $1/T$ in Figure 3. The best straight line (drawn by inspection) is also shown. This line has a slope of −8081 and an intercept of +10.8, thus giving the expression

$$\ln k = -8081/T + 10.8 \qquad (T \text{ in Kelvin})$$

for Henry's constant in this system. The results of Rahmel and Kruger (*1*) are also shown plotted in Figure 3 for comparison.

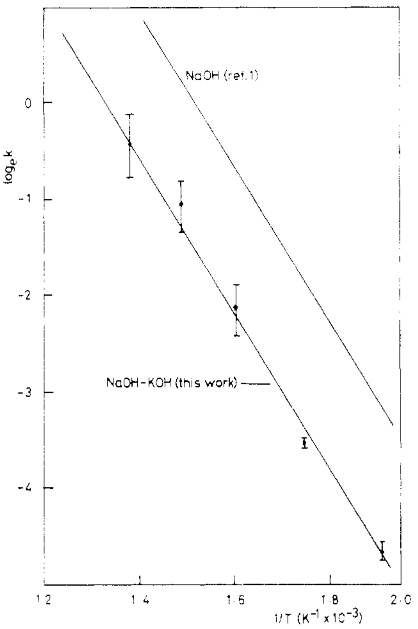

Figure 3. ln of Henry's constant against reciprocal temperature.

Conclusion

The results in Figure 3 show that the eutectic NaOH–KOH contains more water when saturated at a given temperature than does the pure melt NaOH. This is to be expected from the common observation that KOH is more hygroscopic than is NaOH. The fact that the slopes of the two are approximately equal is good evidence for consistency between the present results and those of Rahmel and Kruger. A further development of this work might be to measure the value of the constant in pure KOH to see if the results for the eutectic system lie at values simply related to the composition of the mixture.

Registry No. Water, 7732-18-5; potassium hydroxide, 1310-58-3; sodium hydroxide, 1310-73-2.

Literature Cited

(1) Rahmel, A.; Kruger, H. J. *Z. Phys. Chem. (Wiesbaden)* **1967**, *55*, 25–32.
(2) Hoyt, E. B. *J. Chem. Eng. Data* **1967**, *12*, 461–4.
(3) Coombes, R. In "The Solution Chemistry of Water in Melts"; Inman, D., Lovering, D. G., Eds.; Plenum Press: New York, 1981; Chapter 15, p 309.
(4) Janz, G. J. "Molten Salts Handbook"; Academic Press: New York, 1977; Chapter 1.
(5) Weast, R. C., Ed. "Handbook of Chemistry and Physics", 60th ed.; CRC Press: Boca Raton, FL, 1980; p D196.

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