

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

^aThe freezing point and transition point are apparently superimposed as only one halt in the cooling curve was found.

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-K₂CO₃ 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

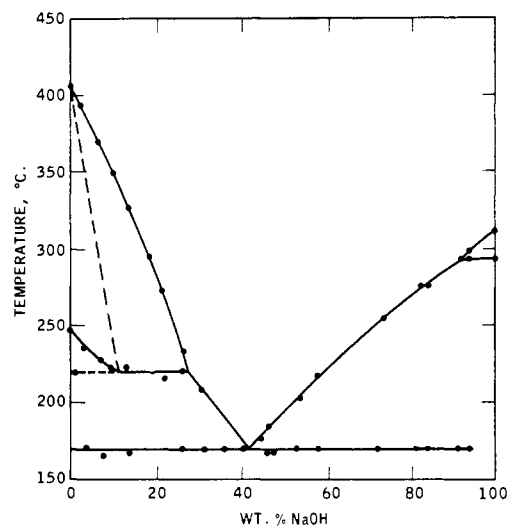


Figure 1. Solid-liquid equilibrium in the KOH-NaOH system

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.

LITERATURE CITED

- (1) Douglas, T.B., Dever, J.L., *J. Res. Natl. Bur. Std.* **53**, 81 (1954).
- (2) Hevesy, G., *Z. Physik. Chem.* **73**, 667 (1910).
- (3) Reshetnikov, N.A., Unzhakov, G.M., *C.A.* **49**, 11382b (1955); *Izvest. Fiz.-Khim. Nauch.-Issledovatel. Inst. Irkutsk. Univ.* **2**, 5-9 (1953).

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

Refractive Index of Phosphoric Acid Solutions at 25° C.

O. W. EDWARDS, R. L. DUNN, and J. D. HATFIELD
Tennessee Valley Authority, Wilson Dam, Ala.

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 4M 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 refrac-

tive increment over the concentration range 0.04 to 16M (0.4 to 90% H₃PO₄). From these data were obtained refractive indexes at 25° C. and 5460.7 Å. 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

For phosphoric acid solutions, $n = 1.333977 + 0.001999w^{1/2} + 0.07155w + 0.0868841w^{3/2} - 0.2375104w^2 + 0.3625678w^{5/2} - 0.1669960w^3$, where n = refractive index at 25° C. and 5460.7 Å. and w = concentration, weight fraction, of H_3PO_4 over the range 0–0.90. The data show that, over the small concentration increments used in measurements of the diffusion of phosphoric acid solutions, n is virtually a linear function of concentration, so that a solution of Fick's diffusion equation based on the linear assumption is valid for the concentration increments used in the measurements.

index results in a series of interference fringes that move as diffusion progresses. The total number of fringes, j_m , depends on the difference in refractive index (refractive increment) of the two solutions. The operation of the instrument and the procedure for photographing and analyzing the interferograms are described by Gosting and coworkers (5, 8).

Wendt and Gosting (11) assumed that the relation between refractive index and concentration for aqueous lactamide solutions up to 2M could be expressed by a fourth-degree equation, and they determined the constants in the equation from the observed refractive increments of Gouy measurements. Similarly, the power series equation, which is extended until it represents the data adequately, was assumed to be applicable to phosphoric acid solutions

$$n = b_0 + b_1x + b_2x^2 + b_3x^3 + \dots \quad (1)$$

where n is the refractive index, each b is an empirical constant, and x is any convenient unit of concentration.

The refractive increment, Δn , is represented by the equation

$$\Delta n = b_1(x_B - x_T) + b_2(x_B^2 - x_T^2) + b_3(x_B^3 - x_T^3) + \dots \quad (2)$$

where the subscripts B and T refer to solutions below and above the boundary, respectively.

Equation 2 was fitted to the data of Table I of reference (4) by a least-squares procedure. The best fit to the 22 points was obtained with a series in $w^{1/2}$ (w = weight fraction H_3PO_4 , %/100), and a single equation was applicable over the entire range of concentration studied.

$$n = 1.333977 + 0.0019993w^{1/2} + 0.0715540w + 0.0868841w^{3/2} - 0.2375104w^2 + 0.3625678w^{5/2} - 0.1669960w^3 \quad (3)$$

The first constant is the refractive index of water (air standard) at 25° C. with the mercury line ($\lambda = 5460.7$ Å.) (9).

Equation 3 reproduced the measurements with a standard deviation of 0.0000048 in Δn in the concentration range 0 to about 6% H_3PO_4 . This precision of Δn corresponds entire range of concentration, 0 to 90% H_3PO_4 , Equation 3 reproduces the measurements with a standard deviation of 0.000015 in Δn , or 0.68 fringe. Although j_m can be determined with greater precision than ± 0.68 for any two solutions, uncertainties in knowledge of the concentrations, and consequently of ΔC , perhaps contribute more to variation in j_m than does the error in determining j_m . Over-all refractive indexes calculated from Equation 3 should be accurate to 1 or 2 units in the fifth decimal place.

The relation between w and C (concn., M H_3PO_4) is

$$w = 0.097995C/\rho \quad (4)$$

in which ρ is density, grams/ml. Values of ρ (1) are related to C by the following equations.

Concentration Range of H_3PO_4

w , Wt. fraction	Molarity, C	
0–0.10	0–1	$\rho = 0.99707 + 0.000880C^{1/2} + 0.052086C - 0.001071C^{3/2}$ (5)
0.10–0.50	1–7	$\rho = 0.99707 + 0.001031C^{1/2} + 0.051341C - 0.0002306C^{3/2} - 0.0002492C^2$ (6)
0.50–0.89	7–16	$\rho = 0.99707 + 0.008600C^{1/2} + 0.0439270C + 0.0021786C^{3/2} - 0.00051024C^2$ (7)

These equations reproduce the measured densities with standard deviations of 0.00002 for Equation 5, 0.00006 for Equation 6, and 0.00004 for Equation 7.

If the refractive index is a linear function of C over the range of concentration, ΔC , in the diffusion cell, the solution of Fick's diffusion equation is greatly simplified (6). This requirement is met for phosphoric acid, within the accuracy of Equation 3, for all solutions in Table I of reference (4)—that is, when the top, except the most dilute solution of the diffusion cell is water. The slope, dn/dC , of the curve represented by Equation 3 as modified by Equation 4 is indeterminate at $C = 0$, but is 0.01706 at $C = 0.001$ and decreases to 0.01051 at $C = 0.01$ and then only to 0.00971 at $C = 0.02$. With further increase in C , the slope decreases more and more slowly and with no inflections, and is 0.00474 at $C = 16$. The curve is essentially linear for the short segments of ΔC given in column 2 of Table I of reference (4). The maximum deviation from linearity over these segments is 0.00005 in n when water is the top solution of the diffusion cell; with all other pairs of solutions the deviation from linearity is less than 0.00001 in n .

LITERATURE CITED

- Christensen, J.H., Reed, R.B., *Ind. Eng. Chem.* **47**, 1277 (1955).
- Dismukes, E.B., Alberty, R.A., *J. Am. Chem. Soc.* **75**, 809 (1953).
- Downing, R.B., Pearson, D.E., *Ibid.* **83**, 1718 (1961).
- Edwards, O.W., Huffman, E.O., *J. Phys. Chem.* **63**, 1830 (1959).
- Gosting, L.J., *J. Am. Chem. Soc.* **72**, 4418 (1950).
- Gosting, L.J., Fujita, H., *Ibid.* **79**, 1359 (1957).
- Gosting, L.J., Hanson, E.M., Kegeles, G., Morris, M.S., *Rev. Sci. Instr.* **20**, 209 (1949).
- Gosting, L.J., Morris, M.S., *J. Am. Chem. Soc.* **71**, 1998 (1949).
- Tilton, L.W., Taylor, J.K., *J. Research Natl. Bur. Standards* **20**, 419 (1938).
- Wagner, B., "Tabellen zum Eintauchrefraktometer," Sonderhausen, 1907.
- Wendt, R.P., Gosting, L.J., *J. Phys. Chem.* **63**, 1287 (1959).

RECEIVED for review February 14, 1964. Accepted May 13, 1964.