Vapor Pressure of Ammonia in Aqueous Potassium Hydroxide Solutions

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The solubility of ammonia, near one atmosphere of partial pressure, is evaluated in 5.35 molal potassium hydroxide solutions from 30° C. to 80° C.

THE VAPOR PRESSURE of ammonia in water is increased by the presence of dissolved potassium hydroxide. This increase has been studied in the past at a limited number of temperatures and concentrations by several workers (*1*, *3*, *6*, *8*), from 25° C. to 60° C., with ammonia concentrations around 1*M* and with potassium hydroxide concentrations usually less than 1.5*M*. These data are not very complete on the effect of temperature on the ammonia vapor pressure, and they are insufficient for an evaluation of the differential heat of solution of ammonia in aqueous KOH.

To extend these data regarding the vapor pressure of ammonia over aqueous KOH–NH_3 solutions to higher temperatures and concentrations, and to obtain further information of the thermodynamic properties (*7*) and the ammonia at known vapor pressures is determined in 5.35*m* KOH solutions from 30° C. to 80° C. The available data are also used to check the applicability of the Setschenow equation (*9*).

$$\log (S/S_o) = kC \qquad (1)$$

The ratio S/S_o is the ratio of the ammonia solubility in potassium hydroxide solution of concentration C to the solubility in pure water, S_o; k is a constant.

EXPERIMENTAL

Ammonia is bubbled for one hour into a three necked, 500ml. Pyrex flask which contains 100ml. of 5.35*m* KOH and which is fitted with a reflux condenser and a ther-

Table I. The Partial Vapor Pressure Data of Ammonia in Aqueous, 5.35 Molal Potassium Hydroxide Solution

Temp., ° C.	Ammonia Conc. Gms./Liter	Atm. Pres. in Mm. of Hg	Vapor Pres.[a], of Water Over 5.35 Molal KOH in Mm. of Hg	Vapor Pres. of Ammonia Mm. of Hg	Bunsen Absorption[b], Coefficient, α, in atm.$^{-1}$
30	74.16	762.80	18.50	744.30	98.21
30	70.86	762.87	18.50	744.37	93.85
40	49.55	762.98	32.8	730.18	66.89
40	50.43	762.93	32.8	730.13	68.25
50	39.54	764.04	53.3	710.74	54.83
50	40.62	763.97	53.3	710.67	56.34
60	24.21	764.10	89.6	674.50	35.40
60	26.58	764.17	89.6	674.57	38.85
70	20.86	764.28	138.0	626.28	32.84
70	19.71	764.22	138.0	626.22	31.02
80	12.63	764.40	215.0	549.40	22.66
80	13.60	764.34	215.0	549.34	24.41

[a] (5). [b] 22.09 liter/mole NH_3 at S.T.P.

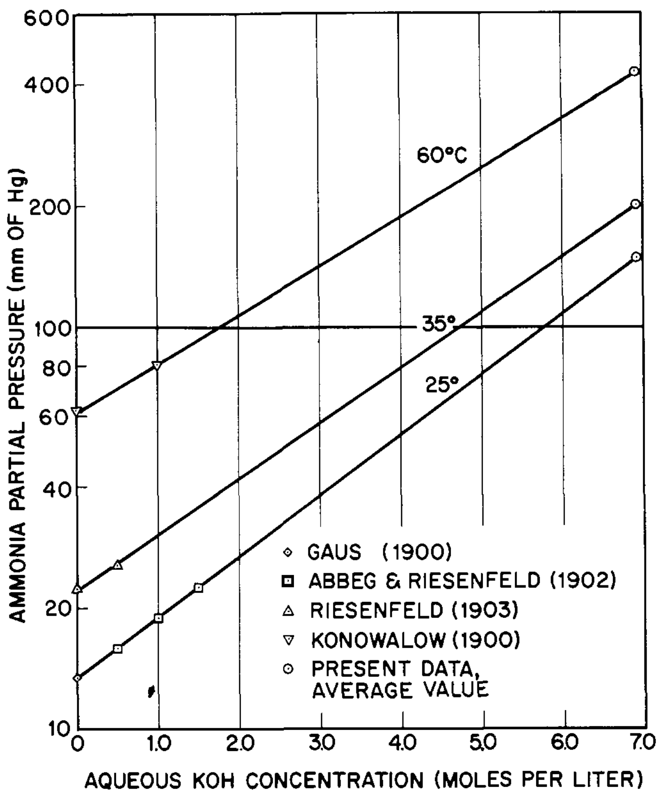

Figure 1. Partial pressure of 1 molar ammonia in aqueous potassium hydroxide solutions at 25° C., 35° C. and 60° C.

mometer. Bubbles do not form in the KOH solution until a degree of ammonia solution occurs. After smooth bubbling occurs, the gas flow is continued for at least one hour at about 200 cc./min. In checks of this work, a variation in the time of bubbling from 1 to 4 hours did not result in a change in the ammonia solution concentration to within the estimated experimental precision, ±5 per cent.

The 500ml. flask is immersed in a large water bath which is thermostated to ±0.1° C. A 5 or 10ml. sample is withdrawn by pipette and introduced into 15ml. of distilled water in a Kjeldahl distilling system. The ammonia is distilled into a known volume of standardized 0.1*N* HCl which is subsequently back titrated with standardized 0.1*N* NaOH to a methyl red endpoint as in a usual ammonia determination. The atmospheric pressure is measured with a mercurial barometer, and the potassium hydroxide concentration is determined from specific gravity measurements in the absence of ammonia (*2*).

RESULTS AND DISCUSSION

The results are collected in Table I. Each line gives the data for a freshly prepared solution. The vapor pressure of water is considered to be lowered negligibly by the presence of ammonia as compared to the lowering by the potassium hydroxide (*5*, *10*). A plot of the log of the Bunsen coefficient, ln α, *vs.* $1/T$ gives a straight line which is used to estimate the differential heat of ammonia solution in 5.35*m* KOH as $\Delta H^\circ_{298} = -6{,}040$ cal. with an estimated deviation of ±400 cal.

$$\ln(\alpha_2/\alpha_1) = -\Delta H/R[1/T_2 - 1/T_1] \qquad (2)$$

The free energy of solution and entropy of solution of ammonia in 5.35*m* KOH may also be estimated (*7*): $\Delta F^\circ_{298} = -830$ cal. and $\Delta S^\circ_{298} = -17.5$ e.u. with an estimated deviation of ±40 cal. and ±2 e.u., respectively.

If the potassium hydroxide concentration, in moles/liter, is plotted *vs.* the log of the ammonia partial pressure over 1*M* NH_3, favorable agreement of the present results is obtained with those of the early workers (*1*, *3*, *6*, *8*). The plot of lnα *vs.* $1/T$ is used to evaluate average α's at 25° C., 35° C., and 65° C., and these α's are used to calculate the vapor pressure of ammonia over a 1*M* NH_3 solution.

In Figure 1, a straight line is obtained which connects Abegg and Riesenfeld's values of log $\bar{P}_{NH_3}$ at 0, 0.5, 1.0 and 1.5*M* KOH (*1*) with the 5.35*m* (6.90*M*) value of Table I, all at 25° C. These agreements permit the formulation of the following expression:

$$\log(P_1/P_2) = k(C_1 - C_2) \qquad (3)$$

where P is the partial pressure of ammonia in mm. of Hg over 1*M* NH_3 in KOH of concentration C, in moles/liter. The constant k is 0.144 liter/mole at 25° C. The Setschenow relation (*9*) is thus shown to be verified after substitution of the Henry law expression into Equation 3.

From the results at other temperatures, 35° C. and 60° C., where linear plots of log P *vs.* C are obtained with the available data, k is found equal to 0.141 liters/mole and 0.125 liters/mole, respectively, and the temperature dependence of the constant k is approximately given by:

$$k_1/k_2 = T_2/T_1 \qquad (4)$$

where T is the absolute temperature in ° K.

Equations 1, 3 and 4 would appear to be generally useful in extrapolations of the published data (*1*, *3*, *4*, *6*, *8*, *10*) to enable estimations of ammonia solubility and vapor pressure values not available in the literature.

The experimental method described should find application in extending the information on the solubility and partial pressure of ammonia in aqueous solutions of KOH.

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