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Ionization Equilibria in Ammonia–Water Solutions to 700° and to 4000 Bars of Pressure

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The electrical conductances of 0.0100 and 0.0501 *m* aqueous ammonia solutions were measured to 800° and 4000 bars. Measurements are also reported for 0.0098 *m* NaOH solutions to 300°, together with estimates of $\Lambda_0(\text{NaOH})$ over the same temperature range. From the measurements on the ammonia solutions and estimates of the limiting equivalent conductances of ammonium hydroxide, conventional equilibrium constants for the hydrolysis of ammonia were calculated. From these values and their isothermal variation with the concentration of water, the complete constants, K^0 , were obtained that are independent of changes in dielectric constant or in density.

Introduction

A convenient method for studying equilibria involving ions in aqueous electrolyte solutions at supercritical temperatures and pressures is the measurement of their electrical conductances. Equilibrium constants for ionic dissociation reactions have been calculated from measurements of this kind over wide ranges of temperature and density. Recent studies in our laboratory have included those of NaCl,^{2a} NaBr,^{2b} and HBr.³ This present paper gives conductance measurements on 0.01 and 0.05 *m* solutions of ammonia to 700°. Measurements were also performed at 800°, but the conductances at this temperature were essentially zero even at 4000 bars. From these measurements and with estimates for the limiting equivalent conductance of $\text{NH}_4^+ + \text{OH}^-$ at several temperatures and densities, conventional equilibrium constants for the hydrolysis of ammonia were calculated to 700°.

The present paper also includes some measurements on 0.0098 *m* NaOH solutions to 300°. From these measurements, estimates were made of the limiting equivalent conductances of NaOH as a function of density to 300°. By using these limiting conductances along with assumptions based on the previously observed behavior of other strong electrolytes at high temperatures and pressures, estimates were made of the limiting equivalent conductance of NaOH to 800°.

Experimental Section

The equipment and procedures used for these mea-

surements have been described previously.^{2a} All conductance measurements were made with the cell containing no pressure seals in the high-temperature region. A stock solution of approximately 1 *m* ammonia was prepared from reagent grade ammonium hydroxide (J. T. Baker Chemical Co., Phillipsburg, N. J., 30% NH_3) and conductivity water. This stock solution was standardized, by using weight buret techniques, against potassium acid phthalate. From the stock solution, 0.0100 and 0.0501 *m* ammonia solutions were prepared and their conductances were measured to 800° and 4000 bars.

A 0.0098 *m* NaOH solution was prepared from a standard 1.0 *N* NaOH solution (Fisher Scientific Co., Fair Lawn, N. J.) and standardized in the same manner as described for the stock solution of ammonium hydroxide. Reliable measurements on the NaOH solution were obtained only at temperatures below 300°. At 400° and above, the solution concentration changed rapidly because of the reaction of NaOH with the Al_2O_3 insulation tube in the high-temperature region of the cell. Thorough flushing of the conductance cell was carried out at the temperature and pressure of the experiment, but even then reliable values of conductances could not be obtained above 300°.

(1) Research sponsored by the U. S. Atomic Energy Commission under contract with Union Carbide Corporation.

(2)(a) A. S. Quist and W. L. Marshall, *J. Phys. Chem.*, **72**, 684 (1968); (b) A. S. Quist and W. L. Marshall, *ibid.*, **72**, 2100 (1968).

(3) A. S. Quist and W. L. Marshall, *ibid.*, **72**, 1545 (1968).

Two different inner electrodes were used with the conductance cell. Their cell constants were 0.495 and 0.525 cm^{-1} as determined from measurements on 0.01 Demal KCl solutions at $25.00 \pm 0.01^\circ$. Conductivity water obtained from a quartz still was used to prepare all solutions.

The experimental measurements on these alkaline solutions were not as accurate as those for the previous electrolytes.^{2,3} Reaction with the Al_2O_3 tube, mentioned above, and pickup of CO_2 from the air in transferring these solutions from the stock bottle to the apparatus introduced errors not found in studying acidic or neutral solutions. Also, with the ammonia solutions the conductances were very low at high temperatures, and therefore the effects of ionic impurities became appreciable. Thus, although the measurements at low temperatures can be considered reliable to within approximately 2%, the uncertainty was much greater at high temperatures and low pressures.

Results and Discussion

Results. The measured conductances were converted to both specific and equivalent conductances by the methods described previously.^{2a} Figures 1 and 2 show specific conductances of the ammonia solutions as a function of pressure at the temperatures of the experiments. Figure 3 presents isobaric specific conductances as a function of temperature for a 0.0100 m ammonia solution. The maxima in these curves near 150° and the subsequent sharp decrease with increasing temperature as compared with the behavior of NaCl ^{2a} and NaBr ^{2b} indicate that these solutions contain relatively few ions at high temperatures. Hydrolysis constants for ammonia were calculated and are presented in a later section of this paper.

Figure 4 gives isotherms of equivalent conductances as a function of density for the 0.0501 m ammonia solution. Again, comparison of these results with the NaCl and NaBr data² indicates that aqueous ammonia is an extremely weak electrolyte at high temperatures. Tables I and II contain smoothed values of the conductances of the ammonia solutions at integral temperatures and densities. The values in parentheses represent conductances at saturation vapor pressure at that temperature.

Figure 5 presents the results for the NaOH solutions, given as the specific conductance as a function of pressure at temperatures to 285° . From these measurements, NaOH appears to behave as a strong electrolyte at least to 300° . Equivalent conductances of 0.0098 m NaOH at integral temperatures and densities are given in Table III.

Estimation of the Limiting Equivalent Conductances of NH_4OH and NaOH to 800° . Limiting equivalent conductances for ammonium hydroxide could not be calculated from the experimental measurements. Since it is a very weak electrolyte, accurate measurements

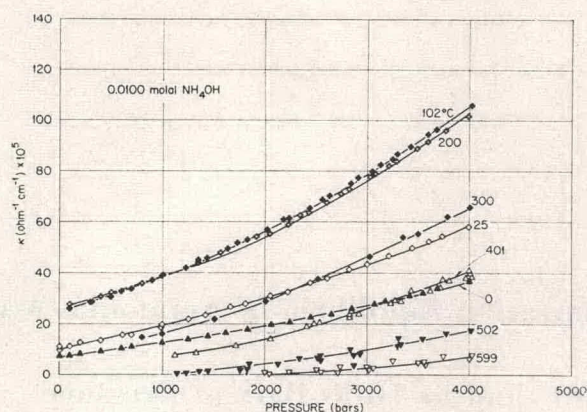


Figure 1. Specific conductances of 0.0100 m solutions of NH_4OH as a function of pressure at several temperatures.

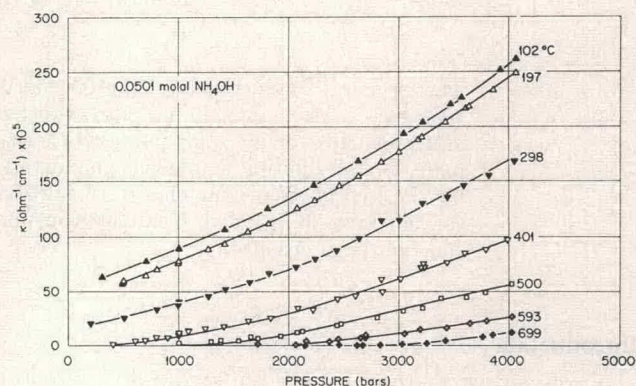


Figure 2. Specific conductances of 0.0501 m NH_4OH solutions as a function of pressure at several temperatures.

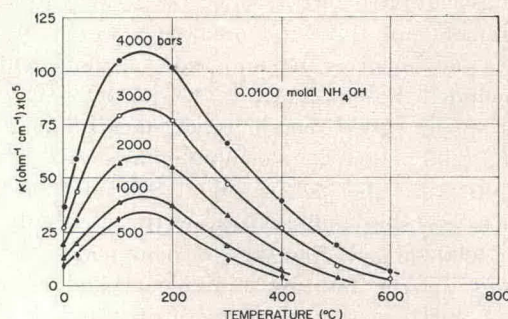


Figure 3. Isobaric variation of specific conductances of 0.0100 m NH_4OH solutions as a function of temperature. Pressures of 500 to 4000 bars.

could not be made at low enough concentrations to permit reliable extrapolations of the conductances to infinite dilution. Therefore, the limiting equivalent conductances for ammonium hydroxide necessary for the calculation of ionization constants from the conductance measurements were obtained indirectly. Estimates of $\Lambda_0(\text{NH}_4\text{OH})$ were calculated as described below and were based primarily on assumed similarities in the behavior of $\Lambda_0(\text{NaOH})$ and $\Lambda_0(\text{NH}_4\text{OH})$.

Table I: The Equivalent Conductances ($\text{cm}^2 \text{ ohm}^{-1} \text{ equiv}^{-1}$) of 0.0100 *m* NH_4OH Solutions at Integral Temperatures and Densities

Temp, °C	Density, g cm^{-3}									
	0.70	0.75	0.80	0.85	0.90	0.95	1.00	1.05	1.10	1.15
0							7.1	13.0	22.5	36.0
25						(10.7)	11.0	21.5	39.7	
100						(25.0)	38.4	66.6	113	
150						...	56.0	
200					31.0	45.6	70.4			
250					33.6	52.0	78.8			
300			17.0	23.0	36.4	56.0	83.0			
350			18.4	26.0	39.2					
400	10.0	13.0	18.8	28.8	42.0					
450	8.0	11.0	17.5							
500	6.0	9.0	15.0							
550	...	7.0								
600	...	6.0								

Table II: The Equivalent Conductances ($\text{cm}^2 \text{ ohm}^{-1} \text{ equiv}^{-2}$) of 0.0501 *m* NH_4OH Solutions at Integral Temperatures and Densities

Temp. °C	Density, g cm ⁻³												
	0.50	0.55	0.60	0.65	0.70	0.75	0.80	0.85	0.90	0.95	1.00	1.05	1.10
100										(11.2)	17.5	32	56
150										...	25.5	45	
200								(9.9)	13.1	20.3	32.0	58	
250									15.3	24.3	37.2		
300						5.4	7.7	11.2	17.4	27.6	41.7		
350						5.4	8.0	12.3	19.5				
400	0.2	0.7	1.2	2.0	3.1	5.4	8.2	13.5	21.2				
450	0.2	0.7	1.1	1.9	3.1	5.4	8.6	14.5					
500	0.2	0.7	1.0	1.8	3.0	5.4	8.8	15.5					
550	0.8	1.6	3.0	5.4	9.0						
600	0.6	1.5	3.0	5.4	9.4						
650	0.5	1.4	2.9								
700	0.4	1.2	2.8								

Table III: The Equivalent Conductances of 0.0098 *m* NaOH Solutions at Integral Temperatures and Densities

Temp, °C	Density, g cm^{-3}									
	0.70	0.75	0.80	0.85	0.90	0.95	1.00	1.05	1.10	1.15
0							134	144	142	134
25						(236)	236	239	235	
100						(563)	563	557	547	
200				(908)	904	890	872			
300	(1100)	1090	1085	1074	1060	1050	1040			

Wright, Lindsay, and Druga⁴ reevaluated the conductance measurements of Noyes⁵ on aqueous NaOH solutions to 218° and obtained limiting equivalent conductances at saturated vapor pressures. These Λ_0 values were later extrapolated to 300°.⁶ Estimates of limiting conductances of NaOH from our present data to 300° were obtained by solving the Onsager conductance equation⁷

$$\Lambda = \Lambda_0 - (\alpha\Lambda_0 + \beta)\sqrt{C} \quad (1)$$

for Λ_0 , using the measured equivalent conductance of

0.0098 *m* NaOH . Values for α and β were calculated at each temperature and density from reported dielectric constants⁸ and viscosities^{9,10} of water. These esti-

(4) J. M. Wright, W. T. Lindsay, Jr., and T. R. Druga, Report No. WAPD-TM-204, Bettis Atomic Power Laboratory, Westinghouse Electric Corp., Pittsburgh, Pa., June 1961.

(5) A. A. Noyes, *et al.*, Publication No. 63, Carnegie Institution of Washington, Washington, D. C., 1907.

(6) A. S. Quist and W. L. Marshall, *J. Phys. Chem.*, **69**, 2984 (1965).

(7) L. Onsager, *Physik. Z.*, **28**, 277 (1927).

(8) A. S. Quist and W. L. Marshall, *J. Phys. Chem.*, **69**, 3165 (1965).

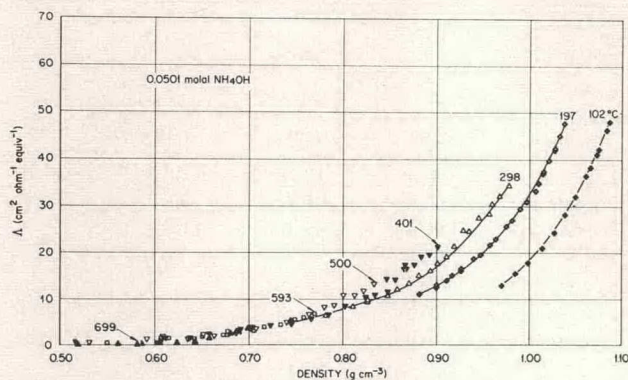


Figure 4. Equivalent conductances of 0.0501 *m* NH_4OH solutions as a function of density at several temperatures.

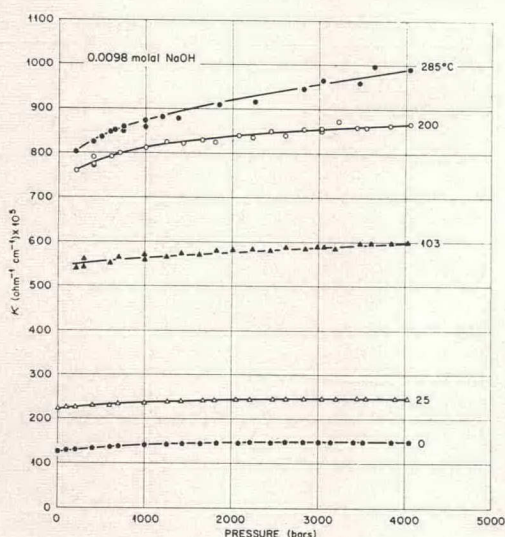


Figure 5. Specific conductances of 0.0098 *m* NaOH solutions as a function of pressure at several temperatures.

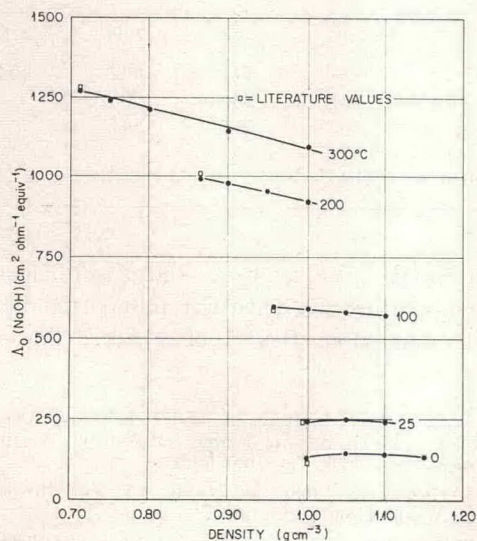


Figure 6. Limiting equivalent conductances of NaOH as a function of density at temperatures from 0 to 300°.

estimated limiting equivalent conductances are shown in Figure 6 as a function of solvent density. The values at saturation vapor pressure agree very well with the previously reported values,⁶ except at 0° where the present values are approximately 7% higher.

The linear relationship between limiting equivalent conductance and density shown in Figure 6 at 100–300° for NaOH has been observed previously at temperatures from 100 to 800° for KHSO_4 ,¹¹ NaCl ,^{2a} NaBr ,^{2b} and HBr .³ Moreover, at temperatures above 400°, the limiting equivalent conductances for several electrolytes^{2,11} have been observed to be independent of temperature at constant density. In these instances, the slope of the line (Λ_0 vs. density) was the same at 400° as at 300°. Therefore, by assuming that NaOH behaves like the previously reported electrolytes, by using the slope of the 300° isotherm from Figure 6, and by using an estimated $\Lambda_0(\text{NaOH})$ at 400° at a particular density, an equation can be written that will give a value for $\Lambda_0(\text{NaOH})$ at all densities at 400° and above. When $\log \Lambda_0(\text{NaOH})$ values at a density of 0.8 and 0.9 g cm^{-3} were plotted against $T(^{\circ}\text{K})^{-1}$ at temperatures to 300° and then extrapolated to 400° in a manner consistent with the observed behavior of NaCl to 400°,^{2a} values of $\Lambda_0(\text{NaOH})$ of 1260 and 1205 were obtained at 400°, 0.8 and 0.9 g cm^{-3} , respectively. With these values, together with the relationship of Λ_0 vs. density observed at 300° (Figure 6), the following equation was obtained to represent the limiting equivalent conductance of NaOH at 400° and above

$$\Lambda_0(\text{NaOH}) = 1770 - 630d \quad (2)$$

where d is the density of the solution.

Limiting equivalent conductances for NH_4OH to 300° were estimated by assuming that the relationship between $\Lambda_0(\text{NH}_4\text{OH})$ and solvent density would be the same as that observed for $\Lambda_0(\text{NaOH})$. From the slopes of the lines for $\Lambda_0(\text{NaOH})$ vs. density at 0–300° shown in Figure 6 and the Λ_0 's for NH_4OH at saturation vapor pressure at these same temperatures,⁶ values of $\Lambda_0(\text{NH}_4\text{OH})$ were calculated and are presented in Table IV. Limiting equivalent conductances at 150, 250, and 350° were obtained by interpolation and extrapolation of plots of $\log \Lambda_0$ vs. $T(^{\circ}\text{K})^{-1}$ (at constant density). Estimates for limiting equivalent conductances of ammonium hydroxide from 400 to 800° are given by the equation

$$\Lambda_0(\text{NH}_4\text{OH}) = 1910 - 630d \quad (3)$$

which was obtained by a procedure similar to that used in calculating the corresponding equation for NaOH (eq 2).

(9) K. H. Dudziak and E. U. Franck, *Ber. Bunsenges. Phys. Chem.*, **70**, 1120 (1966).

(10) K. E. Bett and J. B. Cappi, *Nature*, **207**, 620 (1965).

(11) A. S. Quist and W. L. Marshall, *J. Phys. Chem.*, **70**, 3714 (1966).

Table IV: Estimates of the Limiting Equivalent Conductances of NH_4OH to 350°

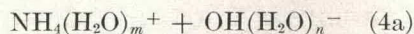
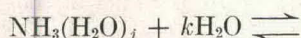
Temp, °C	Density, g cm ⁻³									
	0.70	0.75	0.80	0.85	0.90	0.95	1.00	1.05	1.10	1.15
0							145	155	153	144
25						(272)	272	275	270	
100						(653)	648	640	632	
150						865	835	805		
200				(1095)	1075	1045	1015			
250					1200	1165	1140			
300	(1400)	1375	1345	1310	1280	1250	1220			
350		1420	1385	1355	1325	1290	1260			

Table V: Negative Logarithm of the Conventional Equilibrium Constant, K , for the Hydrolysis of Ammonia in Water [$\text{NH}_3(\text{H}_2\text{O}) \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$]^a

Temp, °C	Density, g cm ⁻³													
	0.50	0.55	0.60	0.65	0.70	0.75	0.80	0.85	0.90	0.95	1.00	1.05	1.10	1.15
0											4.60	4.10	3.55	3.05
25										(4.80)	4.80	4.15	3.55	
100										(4.85)	4.45	3.90	3.35	
150											4.35	3.80		
200								(5.45)	5.20	4.75	4.30	3.75		
250									5.15	4.70	4.30			
300						6.25	5.90	5.55	5.10	4.65	4.25			
350						6.30	5.90	5.50	5.05					
400	9.4	8.3	7.75	7.25	6.75	6.30	5.90	5.40	5.00					
450	9.4	8.3	7.80	7.30	6.80	6.30	5.85	5.35						
500	9.4	8.3	7.90	7.35	6.85	6.35	5.85	5.30						
550	8.10	7.45	6.85	6.35	5.80							
600	8.35	7.50	6.85	6.35	5.75							
650	8.50	7.55	6.90									
700	8.70	7.70	6.90									

^a The standard state is the hypothetical 1 *M* solution.

Calculation of the Hydrolysis Constants for Aqueous Ammonia to 800° . The hydrolysis of aqueous ammonia can be represented by the equations



$$K^0 = \frac{a_{\text{NH}_4(\text{H}_2\text{O})_m} a_{\text{OH}(\text{H}_2\text{O})_n}}{a_{\text{NH}_3(\text{H}_2\text{O})} a_{\text{H}_2\text{O}}^k} \quad (4b)$$

$$K^0 = K/a_{\text{H}_2\text{O}}^k \quad (4c)$$

$$\log K = \log K^0 + k \log a_{\text{H}_2\text{O}} \quad (4d)$$

where K^0 is the complete equilibrium constant, including waters of hydration, and is independent of changes in dielectric constant or in density,^{12,13} K is the conventional equilibrium constant, a represents activity, and j , m , and n are hydration numbers. The conventional constant can be calculated from the experimental data by the equations

$$K = \frac{\theta^2 C_0}{1 - \theta} f_{\pm}^2 \quad (5)$$

$$\ell = \frac{\Lambda}{\Lambda_0} S(z) \quad (6)$$

where θ is the fraction ionized, C_0 is the stoichiometric NH_3 molarity, $S(z)$ is a function defined by Shedlovsky¹⁴ that is based on an empirical extension to the Onsager limiting-conductance equation, and f_{\pm} is the mean molar activity coefficient of NH_4^+ and OH^- calculated by the equation

$$\log f_{\pm} = \frac{-AI^{1/2}}{1 + I^{1/2}} \quad (7)$$

In eq 7, A is the theoretical Debye-Hückel limiting slope for a 1:1 electrolyte and I is the ionic strength calculated from the equation

$$I = \theta C_0 \quad (8)$$

(12) W. L. Marshall and A. S. Quist, *Proc. Nat. Acad. Sci.*, **58**, 901 (1967).

(13) A. S. Quist and W. L. Marshall, *J. Phys. Chem.*, **72**, 1536 (1968).

(14) T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938).

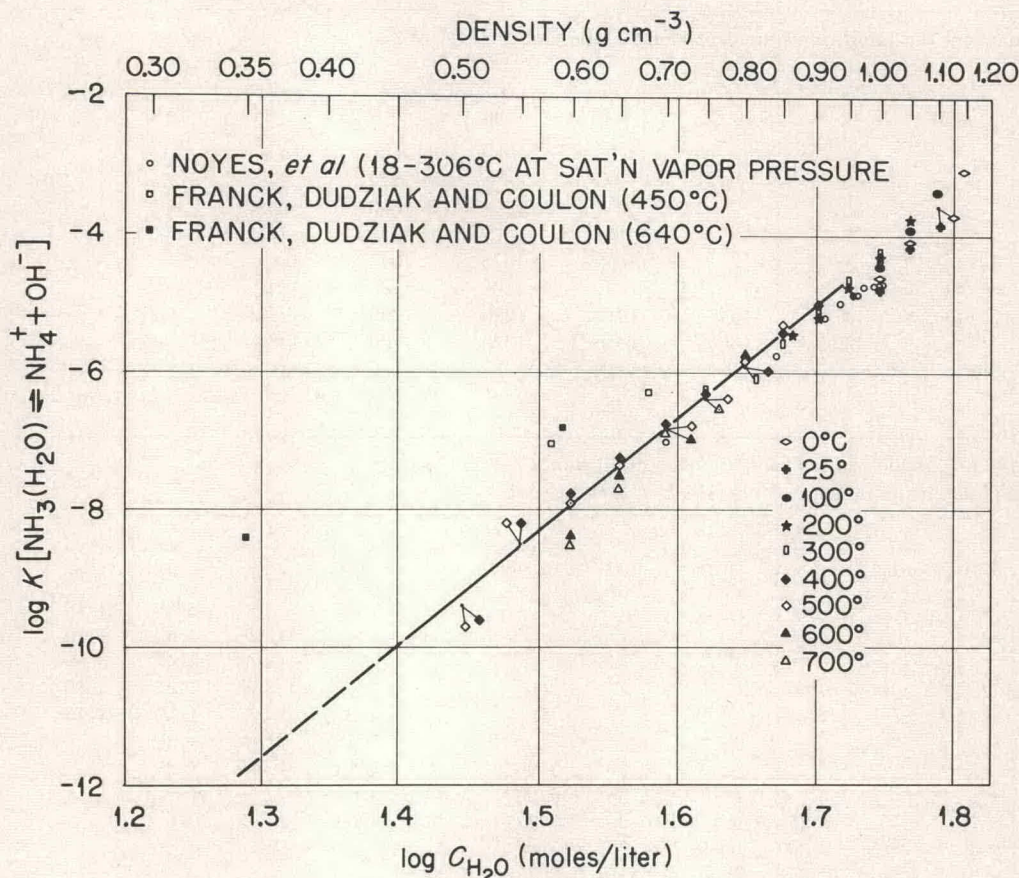


Figure 7. $\log K$ (molar units) for the equilibrium $\text{NH}_3(\text{H}_2\text{O}) \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$ as a function of the logarithm of the molar concentration of water at temperatures from 0 to 700°.

In order to obtain the best value of K when it was calculated from more than one concentration of NH_4OH , the above equations were used in the form¹⁴

$$\frac{1}{\Lambda S(z)} = \frac{1}{\Lambda_0} + \frac{C_0 \Lambda S(z) f_{\pm}^2}{K \Lambda_0^2}$$

A nonlinear least-squares method¹⁵ was used to fit the data to the above equation. Values of the negative logarithm of the conventional equilibrium constant for the hydrolysis of ammonia calculated from the equivalent conductances in Tables I–II (and by using the $\Lambda_0(\text{NH}_4\text{OH})$ values from Table IV and eq 3) are given in Table V. Since the $\Lambda_0(\text{NH}_4\text{OH})$ values are estimates, it is of interest to consider the effect of a change in Λ_0 upon the calculated K . In general, it was found that a 10% decrease in Λ_0 caused approximately a 20% increase in K .

If the activity of water in eq 4d is taken to be equal to its molar concentration,^{12,13} then isothermal plots of $\log K$ vs. $\log C_{\text{H}_2\text{O}}$ (where $C_{\text{H}_2\text{O}}$ is the molar concentration of water) might give straight lines with slope k . This behavior is observed generally, as shown in Figure 7. The slopes of the isotherms decrease with increasing temperature, but seem to reach a constant value near 16–17 between 400 and 500°. Values of k of

31, 29, 25, 21, and 18 were obtained for temperatures of 0, 25, 100, 200, and 300°, respectively. Previously, NaCl was found to have a constant value of k equal to 10.2 from 400 to 800°. For HBr this value of k increased from 12 to 16 with increasing temperature from 400 to 800°.

By using a constant value of $k = 16.5$, values of the logarithm of the complete constant K° were calculated to be -34.0 , -33.0 , -32.9 , and -33.1 at temperatures of 400, 500, 600, and 700°, respectively. These results indicate that ΔE_v° approaches zero at temperatures above 400°.

Plots of the conventional $\log K$ vs. $T(^{\circ}\text{K})^{-1}$ at several constant densities are given in Figure 8. The slopes of these lines give some graphic indications of the behavior of ΔE_v° for the complete equilibrium over a wide range of temperature. Thus at low temperatures ΔE_v° will be positive and appears to approach the value of zero at high temperatures. The sharp decrease in $\log K$ above 500° at densities of 0.65 and 0.60 g cm⁻³ is believed not to be real but only gives an indication of the uncertainty in the values of K at high temperatures and low den-

(15) M. H. Lietzke, United States Atomic Energy Commission Report ORNL-3259, Oak Ridge National Laboratories, Oak Ridge, Tenn., 1962.

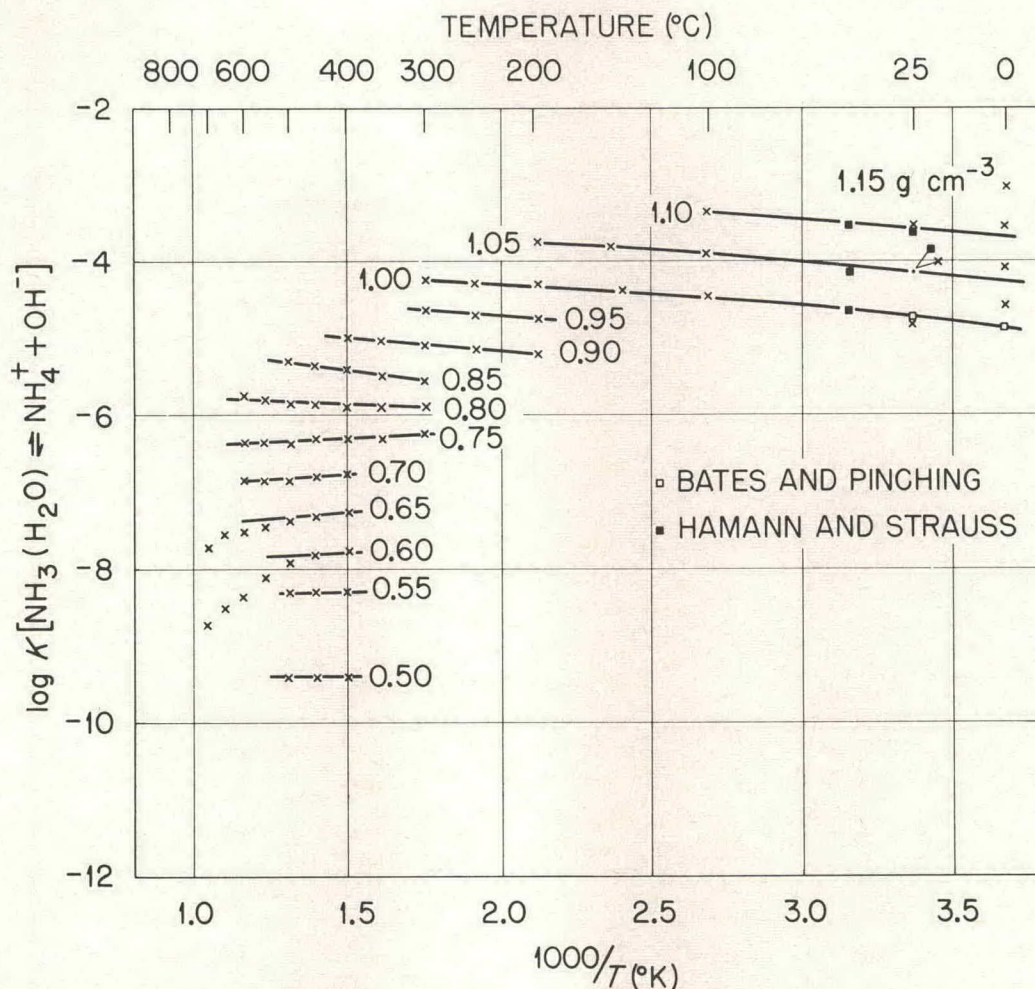


Figure 8. $\log K$ (molar units) for the equilibrium $\text{NH}_3(\text{H}_2\text{O}) \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$ as a function of $T(^{\circ}\text{K})^{-1}$ at solvent densities from 0.50 to 1.15 g cm^{-3} .

sities. It should be noted that in the region (0 – 400°) where k changes with temperature, K° does not represent precisely the same equilibrium at each temperature.³

Previous determinations of the ionization constant of ammonium hydroxide include the results of Bates and Pinching¹⁶ from 0 to 50° at 1 atm by an emf method. Our value of -4.80 for $\log K$ at 25° , 1 atm, agrees well with their value of -4.751 , but our value of -4.60 at 0° , 1 atm, is considerably higher than the Bates and Pinching value of -4.862 . The comparative results are included in Figure 8 and indicate that our own value at 0° may not be reliable. This graph also contains a comparison of our results with those reported by Hamann and Strauss¹⁷ at 25 and 45° at pressures to 12,000 atm; both results are in good agreement. The

present results may also be compared in Figure 7 with values estimated previously by Franck^{18,19} to 640° . Figure 7 also includes the values obtained by Noyes⁵ to 306° at saturation vapor pressure. Our results appear to be in very good agreement with the earlier work of Noyes.

Acknowledgment. The technical assistance of Wiley Jennings in making the conductance measurements is gratefully acknowledged.

(16) R. G. Bates and G. D. Pinching, *J. Amer. Chem. Soc.*, **72**, 1393 (1950).

(17) S. D. Hamann and W. Strauss, *Trans. Faraday Soc.*, **51**, 1684 (1955).

(18) E. U. Franck, *Angew. Chem.*, **73**, 309 (1961).

(19) E. U. Franck, K. H. Dudziak, and G. Coulon, *Abstr. Int. Congr. Pure Appl. Chem.*, 18th, Montreal, 94 (1961).

