Acidic Dissociation Constant of Ammonium Ion at 0° to 50° C, and the Base Strength of Ammonia

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The acidic dissociation of many acids has been studied in detail, but weak bases have generally been neglected because of the experimental difficulties encountered in the investigation of some of their buffer solutions by electromotive-force methods. These difficulties may arise from volatility of the free base or the existence of extraneous electrode reactions such as the formation of ammine complexes at the silver–silver-chloride electrode. In this study of ammonia, special saturators were used to prevent, insofar as possible, the removal of ammonia from the solutions by the hydrogen gas. A correction was applied for the amount of diammine silver complex formed at the silver–silver-chloride electrode, and this silver ion was prevented by mechanical means from reaching the platinum electrodes.

With these precautions, the acidic dissociation constant of ammonium ion at 0° to 50° C was determined from electromotive-force measurements on 19 buffer solutions containing equal molalities of ammonia and ammonium chloride. The changes of free energy, heat content, entropy, and heat capacity that accompany the dissociation processes in the standard state were derived from the temperature coefficients of the acidic dissociation constant of ammonium ion and of the basic dissociation constant of ammonia. The activity coefficient of ammonium chloride in equimolal buffer solutions at 25° C was calculated.

I. Introduction

In principle, the thermodynamic dissociation constants of weak bases in aqueous solution can be determined by the same electromotive-force methods [1, 2, 3][1] that have been used successfully to study the acidic dissociation of a large number of weak acids. The high solubility of silver chloride in solutions of the ammonia bases led Owen to suggest [4] that the silver–silver-iodide electrode be employed. The latter electrode is not, however, as reproducible as the silver–silver-chloride electrode, and its potential is considerably more sensitive to traces of oxygen in the solutions. Furthermore, special precautions must be taken, when the base is volatile, in the use of the hydrogen electrode. In an investigation of solutions of methylamine and its hydroiodide by means of hydrogen–silver-iodide cells, Kanning and Schmelzle [5] found the electromotive force

[1] Figures in brackets indicate the literature references at the end of this paper.

to drift at the rate of about 0.1 mv every 5 min after apparent equilibrium had been attained. They concluded that ". . . the method seems to lack the precision and reproducibility . . . which it enjoys in the study of acid solutions".

The hydrogen–silver-chloride cell is well suited to a determination of the basic dissociation constants of many ampholytes [6] which neither react appreciably with silver chloride nor are removed from the solution by bubbling hydrogen. In solutions of sodium glycinate and sodium chloride, a dilute sodium-amalgam electrode has been found to give results comparable with those obtained with the silver–silver-chloride electrode [7]. There is no theoretical reason why the sodium electrode should not prove applicable to other bases as well. In practice, however, the dropping amalgam electrode is inconvenient at best. The suggestion of Roberts [8] that a thallium amalgam electrode be employed in buffer solutions to which a soluble thallous salt has been

added appears never to have been subjected to experimental test.

Our information concerning the thermodynamics of basic dissociation consists principally of the results of studies of ammonium ion and the mono-methyl-, dimethyl-, and trimethyl-ammonium ions by Everett and Wynne-Jones [9, 10, 11] and of anilinium and chloroanilinium ions by Pedersen [12, 13]. In the work on ammonium and substituted ammonium ions, two hydrogen-electrode half cells, one filled with a mixture of buffer solution and potassium chloride and the second with a solution that differed from the first only by replacement of the buffer by hydrochloric acid, were connected by a bridge of 3.5-N potassium chloride. The liquid-junction potential was eliminated by an extrapolation method and the thermodynamic dissociation constants obtained by an extrapolation to infinite dilution of data for different ionic strengths. Glass electrodes were used by Pedersen in the study of anilinium and chloroanilinium ions.

Inasmuch as our present knowledge of the thermodynamics of weak acids and ampholytes is based chiefly upon the cell with hydrogen and silver–silver-chloride electrodes, it seems desirable that studies of weak bases should relate, insofar as possible, also to this cell. This paper reports a determination of the acidic dissociation constant of ammonium ion from 0° to 50° C by electromotive-force measurements of hydrogen-silver-chloride cells. Suitable precautions were taken to retard the removal of ammonia from the solution and to prevent silver ion from reaching the hydrogen electrodes. Corrections were applied for the solubility of silver chloride in the buffer solutions. The standard changes of free energy, heat content, entropy, and heat capacity for the dissociation of 1 gram ion of ammonium were evaluated. In agreement with Everett and Wynne-Jones [9, 10], log K_a was found to be a linear function of $1/T$, within experimental error, where K_a and T are the dissociation constant and absolute temperature, respectively. The activity coefficient of ammonium chloride in equimolal buffer solutions at 25° C was calculated.

II. Method

Electromotive-force data for cells of the type

Pt; $H_2(g)$, NH_4Cl (m), NH_3 (m), AgCl (s); Ag,

in which m is molality, were obtained. Each emf value, E, corrected to a partial pressure of 1 atm of hydrogen, can be converted to the corresponding value of the acidity function, pwH [14], by the equation

$$\mathrm{pwH} \equiv -\log\ (f_H f_{Cl} m_H) = \frac{\mathbf{F}\,(E - E°)}{2.3026\,RT} + \log\ m_{Cl}, \quad (1)$$

in which $E°$ is the standard potential of the cell; $\mathbf{F}$ is the faraday, 96,496 abs coulombs per equivalent [15]; R is the gas constant, 8.3144 abs j per degree per mole [15]; T is the absolute temperature, $t°$ C$+273.16$; and f is the activity coefficient on the molal scale. The values of $E°$ and of 2.3026 $RT/\mathbf{F}$ in absolute volts are given in table 1. The former were obtained by multiplication of the standard potentials in international volts [16, 17] by the conversion factor, 1.00033 [18].

TABLE 1. *Values of $E°$, 2.3026 $RT/\mathbf{F}$, and K_{sp}/K_I*

t	$E°$	$\dfrac{2.3026\ RT}{\mathbf{F}}$	$(K_{sp}/K_I)\times 10^5$
°C	abs v	abs v	
0	0.23652	0.05419$_5$	2.8
5	.23404	.05518$_5$	2.9
10	.23140	.05617$_8$	2.9
15	.22854	.05717$_0$	2.9
20	.22557	.05816$_2$	3.0
25	.22245	.05915$_4$	2.9
30	.21918	.06014$_6$	2.9
35	.21571	.06113$_8$	2.8
40	.21214	.06213$_0$	2.8
45	.20829	.06312$_2$	2.7
50	.20439	.06411$_4$	2.7
55	.20040	.06510$_6$	
60	.19625	.06609$_8$	

The concentration of hydrogen (hydronium) ion, m_H, is determined by the extent to which the dissociation reaction,

$$NH_4^+ + H_2O = NH_3 + H_3O^+, \quad (2)$$

proceeds. The dissociation constant is formulated

$$K_a = \frac{m_H f_H m_{NH_3} f_{NH_3}}{m_{NH_4^+} f_{NH_4^+} \mathbf{a}_w}, \quad (3)$$

where the molalities, m_i, represent the total molal concentrations of the species i, hydrated or otherwise, and $\mathbf{a}_w$ is the activity of water. If $m_H f_H$ from eq 3 is substituted in eq 1, an expression for $-\log K_a$ is obtained:

$$-\log K_a = \mathrm{pwH} + \log \frac{m_{NH_4^+}}{m_{NH_3}} + \log \frac{f_{NH_4^+} f_{Cl^-} \mathbf{a}_w}{f_{NH_3}}. \quad (4)$$

The last term of eq 4 disappears at zero ionic strength. Consequently, $-\log K_a$ is evaluated in the usual way by plotting the right side of eq 4, computed with a reasonable estimate of the activity coefficients, as a function of ionic strength and extrapolating to infinite dilution where each activity coefficient becomes unity.

1. Correction for Volatility of Ammonia

The gas that surrounds the platinum electrodes of the cells is a mixture of hydrogen, ammonia, and water vapor, and its composition depends upon the temperature and composition of the solution with which it is in equilibrium. Hence, E, the electromotive force of the cell when the partial pressure of hydrogen is 760 mm Hg, is obtained from E', the uncorrected electromotive force, by

$$E = E' + \frac{2.3026\,RT}{2\,\mathbf{F}} \log \frac{760}{P - p_{H_2O} - p_{NH_3}}, \quad (5)$$

where P is the total pressure, and p_{H_2O} and p_{NH_3} are the partial pressures of water vapor and ammonia, respectively.

Inasmuch as an error of 1 mm in the partial pressure of hydrogen changes E by less than 0.02 mv, it is possible to use the vapor pressure of pure water at the appropriate temperature for p_{H_2O} in eq 5, with a resultant error at 50° C of less than 0.05 mv at an ionic strength of 0.5. Similarly, the partial pressure of ammonia is altered so slightly by the presence of ammonium chloride [19, 20] that a negligible uncertainty is introduced in E if p_{NH_3} is taken to be the partial pressure of ammonia vapor in equilibrium with a pure aqueous solution of the same ammonia concentration as that in the buffer solution in question. Henry's law,

$$p_{NH_3} = k m_{NH_3}, \quad (6)$$

appears to be valid for solutions of ammonia in water and in salt solutions of constant ionic strength, at least at ammonia concentrations of a few tenths of a mole per liter or below [19, 21, 22, 23]. The Henry's law constant, k, for partial pressures in mm Hg, appears to be about 12.9 to 13.4 at 25° C [19, 23]. The maximum correction at 25° C, that for the most concentrated buffer solution, amounts to 0.02 mv. The partial pressure of ammonia from aqueous solutions of molal-
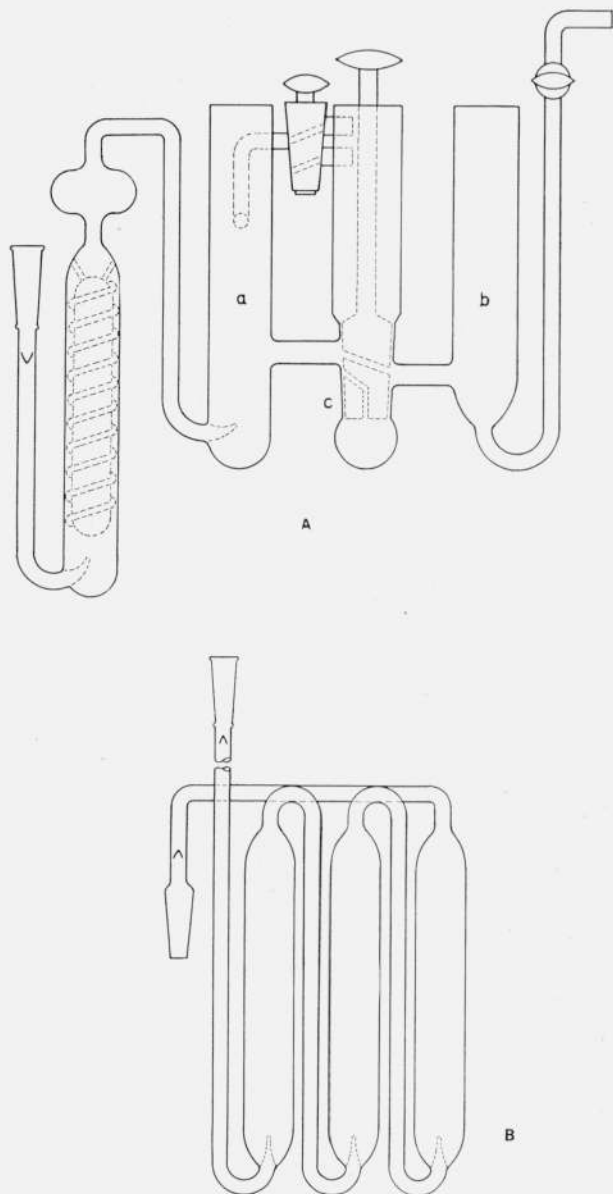

FIGURE 1. *Cell vessel and extra saturator.*

ities exceeding 0.59 is given at several temperatures by Sherwood [24]. From the data for solutions in the range $m = 0.59$ to $m = 1.18$, the Henry's-law constant is found to be 16.3 at 30°, 25.5 to 26.2 at 40°, and 37.8 at 50° C. At 0°, it appears to be 3.8 to 4.0.

No determination of the Henry's-law constant for dilute ammonia solutions seems to have been made at temperatures above 25° C. Consequently, the partial pressure of the gas in equilibrium with a 0.16-m aqueous solution at 50° C was determined by measurement of the amount

of ammonia removed by a definite volume of hydrogen. The solution was contained in a saturator of the type shown at B, figure 1. The saturator was attached by a standard-taper joint to an absorption cell containing 0.01-M hydrochloric acid, which in turn led to a wet-test meter that registered the volume of hydrogen passed through the system. The absorber was designed with two three-way stopcocks to permit the flow of gas emerging from the saturator to bypass the acid solution until air had been swept out of the entire system and equilibrium attained. Then, by a suitable adjustment of the stopcocks, the gas was admitted to the absorption cell through a perforated disk at the bottom. After passage of 0.6 to 1.5 liters of hydrogen, at a rate of about 5 ml per minute, a sample of the acid solution was titrated with 0.008-M sodium hydroxide to the methyl-red endpoint. The accuracy of the method was ascertained by a control measurement of the partial pressure at 25° C. The result, 2.18 mm, compared favorably with 2.06 and 2.14 mm computed from published data [19, 23]. Duplicate measurements at 50° C gave 5.90 and 5.99 mm for the 0.16-m solution, or a value of 37.2 for k, the Henry's-law constant at this temperature. This result can be compared with 37.8 derived from the measurements of Sherwood [24].

2. Correction for Solubility of Silver Chloride

The molality of chloride ion at the silver–silver-chloride electrode is needed to calculate pwH by eq 1. As a result of the appreciable solubility of silver chloride in the buffer solutions, this chloride-ion concentration is somewhat greater than m, the stoichiometric molality of ammonium chloride. Chloride ion and silver enter the solution, the latter principally in the form of the univalent diammine complex ion [25, 26]:

$$AgCl + 2\ NH_3 = Ag\ (NH_3)_2^+ + Cl^-. \qquad (7)$$

The equilibrium constant for reaction 7 is K_{sp}/K_I, where K_{sp} is the solubility-product constant for silver chloride, and K_I is the instability constant for the diammine silver ion. The correction for solubility is made by evaluating the true molality of chloride ion at the silver-chloride electrode for use in eq 1. A secondary effect, the potential gradient through the cell resulting from the small difference of composition between the solutions surrounding the two electrodes, is negligible.

The extent to which reaction 7 proceeds at 25° C is readily calculated from the known values of K_{sp} [27, 28] and K_I [26, 29]. The increase in chloride molality, Δm_{Cl}, will equal the molality of silver-ammonia complex at equilibrium:

$$\Delta m_{Cl} = m_{Ag(NH_3)_2^+} = \frac{K_{sp}}{K_I} \times \frac{(m - 2\Delta m_{Cl})^2 f_u^2}{(m + \Delta m_{Cl}) f_\pm^2}, \qquad (8)$$

where f_u is the activity coefficient of uncharged ammonia molecules and $f_\pm$ is the mean ionic activity coefficient of silver-ammonia chloride. Inasmuch as Δm_{Cl} is a correction that amounts to less than 0.5 percent of m for buffer solutions containing ammonia and ammonium chloride at the same molality (m), where m does not exceed 0.1, it is evident that the actual value need not be established with great accuracy. Indeed, an error of 20 percent in Δm_{Cl} corresponds in the most unfavorable case ($m = 0.1$, 20°C) to less than 0.03 mv in the electromotive force. This error is less than the uncertainty in $E°$ and the reproducibility of the experimental data. Hence, Δm_{Cl} can be omitted from the right side of eq 8, f_u can be considered to be unity, and $f_\pm$ set equal to the mean stoichiometric activity coefficient of hydrochloric acid, f_{HCl}, at the concentration m [6, 16]. With these simplifications, eq 8 becomes

$$\Delta m_{Cl} \approx (K_{sp}/K_I)(m/f_{HCl}^2), \qquad (9)$$

for the special case of equimolal buffer solutions, and eq 1 can be written

$$pwH = \frac{F(E - E°)}{2.3026 RT} + \log m + \log [1 + (K_{sp}/K_I)/f_{HCl}^2]. \qquad (10)$$

At 25° C, the correction for solubility, represented by the last term of eq 10, contributes 0.0020 to pwH for $m = 0.1$ and 0.0015 for $m = 0.01$. Thus the percentage increase in chloride concentration resulting from solution of silver chloride in the buffer solutions is practically independent of m, provided that the ammonia and ammonium chloride are present at equal molalities. It should be remembered that the decrease in ammonia concentration resulting from the formation of complex ion according to reaction 7 is confined to the vicinity of the silver–silver-chloride electrode and, consequently, does not influence the activity of hydronium ion at the hydrogen electrode.

For temperatures other than 25° C, K_{sp} was taken from the paper of Owen and Brinkley [28].

Their equation for the variation with temperature of the logarithm of the solubility-product constant between 5° and 45° C was used to calculate the constant for 0° and 50° C as well as for the intermediate temperatures. By assuming that the heat of formation of the diammine complex from silver ion and ammonia is constant over the range 0° to 50° C and equal to -13.2 kcal, as found by Berthelot and Delépine [30], K_I can be calculated at the other temperatures from its value at 25° C. This procedure is justified by the low degree of precision required. The values of K_{sp}/K_I obtained in this manner are given in the last column of table 1.

3. Correction for Hydrolysis

The base strength of ammonia exceeds the acid strength of ammonium ion. Consequently, these two constituents of equimolal buffer solutions will react with the amphoteric water solvent to different extents, with the net result that a part of the ammonia is converted into ammonium ion:

$$NH_3 + H_2O = NH_4^+ + OH^-. \qquad (11)$$

The concentration of hydroxide ion at equilibrium evidently indicates the extent to which reaction 11 takes place, that is, the number of moles of ammonium ion formed at the expense of an equal amount of ammonia. Hydrolysis is greatest at the highest temperature. However, the correction to $\log K_a$ is only 0.0024 in the most unfavorable case. The molality of hydroxide ion is readily obtained by the approximation [31]

$$\log m_{OH} \approx \log K_w + pwH, \qquad (12)$$

where K_w represents the ionization constant of water [6]. If m is the stoichiometric molality of ammonia and of ammonium chloride, the second term on the right of eq 4 is given by

$$\frac{m_{NH_4^+}}{m_{NH_3}} = \frac{m + m_{OH}}{m - m_{OH}}. \qquad (13)$$

4. The Extrapolation

When this electromotive-force method is applied to a determination of the dissociation constant of an uncharged monobasic acid [3], the term containing activity coefficients is nearly zero in dilute solutions. When the acid is a univalent cation such as ammonium, however, this is not the case. The last term of eq 4 is approximately twice the common logarithm of the mean activity coefficient of ammonium chloride, or about -0.08 for $m = 0.005$ at 0° C [32]. Unfortunately, the activity coefficient of ammonium chloride in these buffer solutions has not been determined. In order to evaluate $\log K_a$, therefore, the activity-coefficient term in the experimental range of concentrations must be expressed as some function of ionic strength, so that an accurate extrapolation can be made to zero ionic strength. The two-parameter equation of Hückel [33] was found to be well suited to this purpose. This same equation successfully represents the corresponding activity-coefficient terms in buffer systems of acid anions.

If each ionic activity coefficient is expressed by the Hückel equation, the last term of eq 4 becomes

$$\log \frac{f_{NH_4^+} f_{Cl^-} \boldsymbol{a}_w}{f_{NH_3}} = \frac{-2A\sqrt{\mu}}{1 + Ba^*\sqrt{\mu}} + \beta\mu, \qquad (14)$$

where A and B are constants at a particular temperature in the water medium [34], a^* and β are adjustable parameters, and μ, the ionic strength, is, for the purpose at hand, negligibly different from the molality of ammonium chloride. This difference was less than 0.6 percent in all cases. The complete equation can now be written in a form for extrapolation by making the appropriate substitutions in eq 4:

$$-\log K_a' \equiv -\log K_a - \beta m = pwH +$$

$$\log \frac{m + m_{OH}}{m - m_{OH}} - \frac{2A\sqrt{m}}{1 + Ba^*\sqrt{m}}. \qquad (15)$$

The a^* parameter governs the curvature of the extrapolation plots. When too large a value of a^* is used, a plot of the right side of eq 15 with respect to m is concave downward; if a^* is too small, the curves are concave upward. A value of 2.0 at each temperature was found to yield straight lines that could be extended with little uncertainty to zero concentration, as shown in figure 2. The slopes of these lines are $-\beta$. From the measured slopes, β was found to have the following values, for $a^* = 2.0$: 0.22 at 0°, 0.27 at 5°, 0.28 at 10° to 40°, inclusive, 0.30 at 45°, and 0.31 at 50° C.
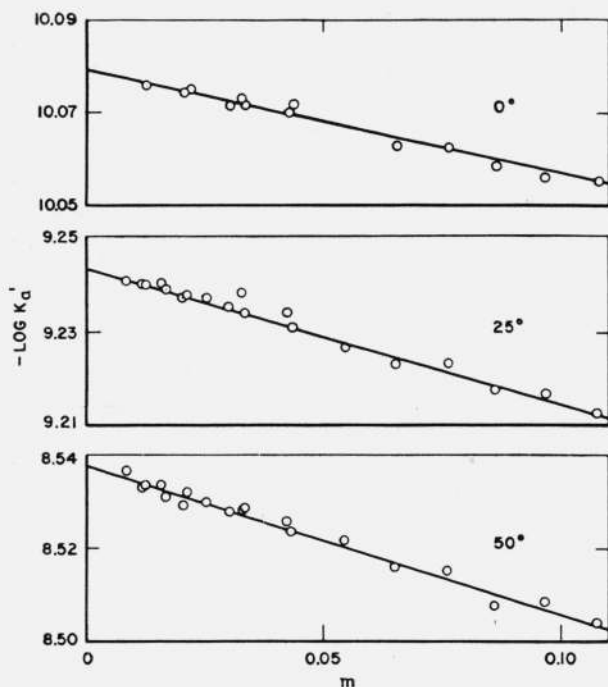
FIGURE 2. *Plot of* $-\log K_a'$, *the right side of eq 15, as a function of m at* $0°$, $25°$, *and* $50°$ C.

III. Experimental Details

From an experimental point of view, it is not sufficient that corrections be made for hydrolysis, for the solubility of silver chloride, and for the partial pressure of ammonia. If the cells are to maintain constant values for periods of 2 to 3 days, two precautions must be observed. First, silver ion must be prevented from reaching the hydrogen electrodes and ammonia from diffusing in the opposite direction to equalize the small difference in concentration between the two electrode solutions. Secondly, removal of ammonia by the bubbling hydrogen must be eliminated, insofar as possible. Both of these difficulties were surmounted by use of the cell shown in figure 1. The solution in the vicinity of the hydrogen-electrode compartment, *a*, is separated from that in the silver-silver chloride electrode compartment, *b*, by a stopcock (*c*) having a bore approximately 4 mm in diameter. Part *B* is a triple saturator containing some of the same buffer solution as the cell. In it the hydrogen gas becomes charged with sufficient ammonia and water vapor to preclude a change in composition of the solution in the hydrogen-electrode compartment. Part *B* is attached to part *A* at the standard-taper joint at the left of the figure.

The intermediate stopcock, open only at the time of measurement, appeared to be essential to constancy of electromotive force. Three cells, two with separation of the electrode compartments and one without, were filled with an equimolal buffer solution of 0.05–*m* ammonium chloride and 0.05–*m* ammonia. All three were provided with the extra saturator. Over a period of 48 hr, the electromotive force of the cells with stopcocks dropped by 0.14 and 0.05 mv, whereas that of the one without a stopcock fell 1 mv, in spite of the fact that a gray cast on the edges of the platinum electrodes was scarcely perceptible. This result was surprising in view of the small effect that visible deposits of silver have been found to exert on the potentials of hydrogen electrodes in certain basic buffer solutions.

Solutions of ammonia, about 0.1–*M*, were prepared in paraffin-lined flasks by absorption of ammonia gas in conductivity water from which dissolved oxygen had previously been removed by passage of a stream of nitrogen. A stream of nitrogen gas was also used to remove ammonia from a concentrated chemically pure solution, contained in a gas-washing bottle, and to conduct it into the flask of water. The concentration of ammonia was determined by weight titration, for which a 0.1–*M* solution of distilled hydrochloric acid, standardized by gravimetric determination of its chloride concentration, was used, with methyl red as indicator. Although the color change was quite sharp, a color standard composed of ammonium chloride solution and indicator aided in establishing the endpoint. The titrations were performed by addition of the ammonia solution to the standard solution of hydrochloric acid. Sufficient pure ammonium chloride to equal the molality of the ammonia was added to this stock solution. Ammonium chloride of reagent grade was purified by a single recrystallization from water. It was dried at 110° C and analyzed by gravimetric determination of chloride. Three analyses gave a result of 100.03±0.01 percent.

In order to avoid loss of ammonia and at the same time exclude atmospheric oxygen and carbon dioxide, the buffer solutions were prepared in the following manner. The proper quantity of pure water was placed in the weighed solution flasks and nitrogen passed through for 2 hr to remove oxygen. The flasks were weighed again,

the stock solution added with the aid of a modification of the apparatus described by Bates and Acree [35], and a final weight obtained. Inasmuch as the solution flasks were already filled with nitrogen, however, it was considered unnecessary to risk loss of ammonia by passing nitrogen into them during addition of the stock solution. "High-vacuum" silicone lubricant appeared to be little affected by the buffer solutions, and a thin film of it was used to lubricate the stopcocks in the cells and solution flasks.

About 6 hr was allowed for the cells to attain their initial equilibrium values of electromotive force at 25° C, although no more than 4 hr was usually necessary. The temperature was lowered to near 0° overnight. Measurements at 0° to 25° were made on the second day and at 25° to 50° on the third day, when final values at 25° were also obtained. A comparison of the four electromotive-force values for each cell at 25° C revealed a slow decrease in potential, roughly linear with time, during the 48-hr course of the experiments. Most of the results obtained near the end of the series, that is, at 25° to 50°, were increased by small amounts in order to compensate for this slow change. No change was made in the data for three cells, twelve were increased by 0.04 to 0.10 mv, and three by 0.10 to 0.15 mv. The electromotive force of the cell containing the most dilute solution (0.008569 m) decreased abnormally, and 0.23 and 0.40 mv were added to the low- and high-temperature data, respectively, for this cell.

IV. Results

The corrected electromotive-force data for each solution over the range 0° to 50° C were fitted to the quadratic equation,

$$E_t = E_{25} - a\ (t-25) - b\ (t-25)^2, \qquad (16)$$

by the graphical method described by Harned and Nims [36]. The constants of eq 16 are given in table 2. The average differences between the "observed" electromotive force at the 11 temperatures and that calculated by eq 16 are given in the last column. It is apparent from the figures in the next to the last column that there is no significant trend of the constant b with change of m. If the mean value of b, 3.1×10^{-6}, were chosen for the computation of E_t for each solution

by eq 16, a maximum error of 0.09 mv, at the extreme temperatures of 0° and 50° C., would be introduced.

TABLE 2. *Electromotive force of the cell:* Pt; H$_2$, NH$_3$ (m), NH$_4$Cl (m), AgCl, Ag; *constants of eq 16*

m	E_{25}	$a \times 10^4$	$b \times 10^6$	Mean ΔE
	abs v			mv
0.10773	0.84090	3.63	3.05	0.03
.09635	.84321	3.55	3.04	.03
.08613	.84548	3.50	3.15	.01
.07620	.84817	3.39	3.04	.03
.06499	.85139	3.30	3.08	.02
ª.05463	.85514	3.15	3.20	.06
.04354	.86004	3.08	3.16	.06
.04272	.86053	3.02	3.20	.03
.03372	.86559	2.84	3.08	.02
.03301	.86613	2.84	3.20	.05
.03017	.86798	2.78	3.12	.04
ª.02540	.87180	2.64	3.16	.03
.02124	.87585	2.52	3.24	.04
.02069	.87625	2.54	2.96	.04
ᵇ.017015	.88077	2.40	3.05	.06
.015834	.88243	2.34	3.12	.07
.012598	.88755	2.16	3.08	.04
ª.011842	.88897	2.16	3.00	.03
ª.008569	.89649	1.94	3.02	.04

ª For the range 5° to 50° C, incl.
ᵇ For the range 25° to 50° C, incl.

The mean values of $-\log K_a$ derived by the methods described in the foregoing section are listed in table 3. These were obtained by averaging the results from the measurement of each individual solution by the equation

$$-\log K_a = -\log K'_a + \beta m, \qquad (15a)$$

where $-\log K'_a$ represents the numerical value of the right side of eq 15 when $a^* = 2$. The values of β have been given in the previous section. The basic dissociation constant of ammonia, K_b, is the equilibrium constant for reaction 11. The constant K_b is evidently K_w/K_a. Hence,

$$\log K_b = \log K_w - \log K_a. \qquad (17)$$

Values of $-\log K_b$ computed from $-\log K_a$ and $\log K_w$[6] are given in the next to the last column of table 3. The third and last columns list K_a and K_b, respectively.

By another electromotive-force method, Everett and Wynne-Jones [9] found 9.215 for $-\log K_a$ at 25° C. This result is appreciably lower than

TABLE 3. *Acidic dissociation constant of ammonium ion, K_a, and the basic dissociation constant of ammonia, K_b*

t	$-\log K_a$	$K_a \times 10^{10}$	$-\log K_b$	$K_b \times 10^5$
°C				
0	10.0813±0.0009	0.829	4.862	1.37
5	9.9040±0.0010	1.247	4.830	1.48
10	9.7306±0.0010	1.860	4.804	1.57
15	9.5641±0.0011	2.73	4.782	1.65
20	9.4002±0.0007	3.98	4.767	1.71
25	9.2449±0.0010	5.69	4.751	1.77
30	9.0926±0.0012	8.08	4.740	1.82
35	8.9466±0.0009	11.31	4.733	1.85
40	8.8047±0.0007	15.68	4.730	1.86
45	8.6700±0.0008	21.4	4.726	1.88
50	8.5387±0.0011	28.9	4.723	1.89

9.244, recorded in table 3. Hence, their value of K_b, 1.65×10^{-5}, is also lower than that (1.77×10^{-5}) found in this investigation. Owen's determination with the silver–silver-iodide electrode [4] gave 1.75×10^{-5}. This corresponds to 9.239 for $-\log K_a$. In earlier work, Harned and Owen [1] calculated 1.79×10^{-5} for K_b from electromotive-force measurements of unbuffered cells [37]. The medium effect amounted, however, to about 20 percent of K_b, and some uncertainty was introduced in correcting for it. Determinations of K_b by the conductance method display a somewhat greater uniformity than do the electromotive-force studies, namely, 1.81×10^{-5} (Kanolt, 1907 [38]), 1.87×10^{-5} (Lundén, 1907 [39]), 1.81×10^{-5} (interpolated; Noyes, Kato, and Sosman, 1910 [40]), and 1.82×10^{-5} (Lewis and Schutz, 1934 [41]), all at 25° C.

V. Thermodynamic Functions for the Dissociation of Ammonia and Ammonium Ion

Everett and Wynne-Jones [9] were able to represent their values of $-\log K_a$ from 5° to 45° C by the simple equation

$$-\log K_a = \frac{A}{T} + B, \qquad (18)$$

where T is temperature in °K and A and B are, respectively, 2,706 and 0.139. The general equation, of which eq 18 is a special case, can be written

$$-\ln K = \frac{A}{T} + B - \frac{\Delta C_p}{R} \ln T, \qquad (19)$$

or

$$-\log K_a = \frac{A}{T} + B + C \log T, \qquad (19a)$$

where ΔC_p, the change of heat capacity for the given process, is assumed to be a constant over the temperature range in question [10, 42]. For the dissociation of ammonium ion, these authors found ΔC_p to be zero. Equation 18 can also be regarded as a special case of the equation

$$-\log K_a = \frac{A}{T} + B + C T, \qquad (20)$$

which is of the form suggested by Harned and Robinson [43]. By application of the usual thermodynamic formulas, it becomes evident that eq 20 requires ΔC_p for the dissociation process to be directly proportional to T, rather than a constant.

The discovery that ΔC_p for the dissociation of ammonium ion is zero was not surprising, in view of the isoelectric character of process 2. Nor would it have been surprising if ΔC_p for the dissociation of other hydrogen acids with a single positive charge were also zero. This expectation has not been fulfilled, however, for studies of the mono-, di-, and trimethylammonium ions have yielded rather large positive values of ΔC_p [10, 11].

The proper equation for the calculation of the thermodynamic functions must be presumed to be the equation that best represents the individual K_a values. Unfortunately, the range of temperatures over which measurements are made rarely exceeds 60° C, and experimental errors usually preclude an accuracy greater than ± 0.002 in $-\log K$. Hence, it is sometimes found that each of two equations representing two different means of smoothing the experimental results reproduces the data equally well. In such a case, there is no way to choose between two different values of the temperature coefficient of log K, and, hence, between different values of the heat content and entropy changes for the dissociation. The differences in the second derivative, upon which ΔC_p depends, will be still larger.

The values of $-\log K_a$ given in table 3 can be represented either by eq 18 or by eq 20 with a mean deviation of 0.0011. The constants of these equations were obtained by the method of least squares and are given in table 4. Harned and Owen [6, 44] examined four determinations of the ionization constant of water and found that $-\log K_w$ between 0° and 60° C can be expressed by

$$-\log K_w = \frac{4470.99}{T} - 6.0875 + 0.017060 T, \qquad (21)$$

with an average deviation of 0.0005. As eq 17 indicates, an expression for $-\log K_b$ is found by subtracting eq 18 from eq 21. The resulting equation, the constants of which are also given in table 4, is in the form of eq 20.

TABLE 4. *Change of K_a and K_b with temperature: constants of eq 18 and 20*

	A	B	C
K_a, eq 18	2727.42	0.0973	....
K_a, eq 20	2835.76	−.6322	0.001225
K_b, eq 20	1743.57	−6.1848	.017060

The thermodynamic functions for the two dissociations (processes 2 and 11) in the hypothetical standard state of unit activity are computed by the equations

$$\Delta F^\circ = 2.3026R(A + BT + CT^2) \qquad (22)$$

$$\Delta H^\circ = 2.3026R(A - CT^2), \qquad (23)$$

$$\Delta S^\circ = 2.3026R(-B - 2CT), \qquad (24)$$

$$\Delta C_p^\circ = 2.3026R(-2CT), \qquad (25)$$

where ΔF° is the standard free-energy change, ΔH° the standard heat-content change, ΔS° the standard entropy change, and ΔC_p° the standard change of heat capacity. When these formulas are used with the constants of eq 18, the terms containing C are omitted.

The four thermodynamic quantities for the acidic dissociation of ammonium ion at 0°, 25°, and 50° C are given in table 5. Two sets of values, computed from the constants of eq 18 and 20, respectively, are included. At 0° and 50° C, the extremes of the experimental range, the uncertainty in ΔH°, ΔS°, and ΔC_p° is large, as the differences between the two methods of computation indicate. In the center of the experimental range, however, the temperature coefficient is established with much greater certainty, and only the values of ΔC_p° differ appreciably at 25° C. The differences at 0° and 50° C serve as a warning against placing undue reliance on the temperature coefficient at the extremes of the temperature span. It is thought that ΔH° is accurate within 300 j mole^{-1} at 25° C and that the uncertainty in ΔS° is less than 1 j deg^{-1} mole^{-1}. For comparison with the results obtained by Everett and Wynne-

TABLE 5. *Thermodynamic functions for the acidic dissociation of ammonium ion:* $NH_4^+ = NH_3 + H^+$

Equation	ΔF°	ΔH°	ΔS°	ΔC_p°
		0° C		
	abs j mole^{-1}	abs j mole^{-1}	abs j deg^{-1} mole^{-1}	abs j deg^{-1} mole^{-1}
18	52,725	52,216	−1.86	0
20	52,733	52,540	−0.70	−13
		25° C		
18	52,771	52,216	−1.86	0
20	52,765	52,205	−1.87	−14
		50° C		
18	52,818	52,216	−1.86	0
20	52,827	51,841	−3.06	−15

TABLE 6. *Thermodynamic quantities for the acidic dissociation of ammonium ion at 25° C compared with the results of Everett and Wynne-Jones*

	ΔF°	ΔH°	ΔS°	ΔC_p°
	cal mole^{-1}	cal mole^{-1}	cal deg^{-1} mole^{-1}	cal deg^{-1} mole^{-1}
Everett and Wynne-Jones [10]	12,562	12,400	−0.54	0
This investigation	12,611	12,478	−.45	0; −3

TABLE 7. *Thermodynamic functions for the basic dissociation of ammonia:* $NH_3 + H_2O = NH_4^+ + OH^-$

t	ΔF°	ΔH°	ΔS°	ΔC_p°
°C	abs j mole^{-1}	abs j mole^{-1}	abs j deg^{-1} mole^{-1}	abs j deg^{-1} mole^{-1}
0	25,407	9,010	−60.0	178
25	27,111	4,345	−76.4	195
50	29,225	−728	−92.7	211

Jones [9, 10], the thermodynamic quantities in joules were converted to numbers of calories by dividing by 4.1840. Table 6 demonstrates the essential agreement between the two investigations. Only in the case of ΔF° are the differences as large as the combined errors of the two determinations.

The thermodynamic constants for the basic dissociation of ammonia are given in table 7. The value of ΔH° (1,040 cal mole^{-1}) can be compared with 855 cal given by Thomsen [45], with 835 cal found by Muller and Bauer [46], and

with 1,157 cal computed by Lundén [39] from his values of K_b obtained by the conductance method.

VI. Activity Coefficients

It is evident from eq 4 that the activity-coefficient term $f_{NH_4^+}f_{Cl^-}(a_w/f_{NH_3})$ can be obtained from the experimental data when K_a is known. This is probably accomplished most conveniently by eq 14. The first part of this term, $f_{NH_4^+}f_{Cl^-}$, is the square of the mean ionic activity coefficient, $f_{\pm}$, of ammonium chloride in the mixtures containing equal molalities of ammonia and ammonium chloride, and the part enclosed in parentheses is the ratio of the activity of water to the activity coefficient of the uncharged ammonia molecules. It must be remembered, however, that $f_{NH_4^+}$, f_{NH_3}, and a_w in eq 14 relate to the solution at the hydrogen electrode where the activity of hydrogen ion, which they influence according to eq 3, exerts its effect upon the potential of the cell. Yet f_{Cl}, as already indicated, is the activity coefficient of chloride ion in the solution immediately surrounding the silver-silver chloride electrode, where chloride exerts its primary effect. Hence, eq 14 should most properly be separated into two parts or, for small differences of composition, mean values of μ and $\mu^{1/2}$ used in the equation as written.

The differences of composition diminish as the ionic strength of the equimolal buffer solutions becomes smaller. For this reason it was permissible, for purposes of extrapolation, to substitute m for μ (eq 15). The ionic strength at the hydrogen electrode is $m+m_{OH}$ and at the silver-silver chloride electrode $m+m_{OH}+\Delta m_{Cl}$. The difference, Δm_{Cl}, is greatest for the most concentrated buffer solution (0.10773 m) and at 0° C. If m were used in place of the average μ to calculate $\log (f_{NH_4^+}f_{Cl^-}a_w/f_{NH_3})$ for this most unfavorable case, an error of only 0.0004 would result. This figure corresponds to 0.03 mv, or less than the experimental error. Hence the use of m in place of ionic strength to compute activity coefficients in the range 0 to 0.1 m involves no compromise of accuracy. Inasmuch as a^* is 2.0 at each temperature, eq 14 can be rewritten

$$\log (f_{\pm}\sqrt{a_w/f_{NH_3}}) = \frac{-A\sqrt{m}}{1+2B\sqrt{m}}+0.5\,\beta\,m. \quad (26)$$

Table 8 gives this activity-coefficient term in six

TABLE 8. *Values of* $f_{\pm}\sqrt{a_w/f_{NH_3}}$ *in six buffer solutions containing equal molalities of ammonia and ammonium chloride*

| t | Molality of ammonia and ammonium chloride | | | | | |
	0.005	0.01	0.02	0.05	0.07	0.1
°C						
0	0.928	0.902	0.869	0.813	0.790	0.764
5	.928	.902	.869	.814	.791	.765
10	.927	.901	.868	.813	.790	.766
15	.927	.901	.867	.812	.789	.764
20	.926	.900	.866	.810	.787	.762
25	.925	.899	.865	.809	.786	.760
30	.925	.898	.864	.807	.784	.758
35	.924	.897	.863	.806	.782	.756
40	.923	.896	.862	.804	.780	.754
45	.923	.896	.861	.803	.780	.752
50	.922	.895	.859	.801	.778	.750

buffer solutions containing equal molalities (m) of ammonia and ammonium chloride at 0° to 50° C. These values were computed by eq 26.

Matthews and Davies [20] determined the activity coefficient of ammonia in solutions containing ammonium chloride by measurement of the distribution of ammonia between water and chloroform at 25° C. From their data it is possible to calculate $\sqrt{f_{NH_3}}$ in two equimolal buffer solutions. For 0.02 m, $\sqrt{f_{NH_3}}$ is 0.999, and for 0.2 m, 1.007. Inasmuch as the change of the activity coefficient with change of m is so small, $\sqrt{f_{NH_3}}$ can doubtless be estimated in the range of molality 0 to 0.1 with an error no greater than ±0.002. The limiting value at $m=0$ is, of course, unity.

Stokes [47] has calculated the activity of water in solutions of potassium chloride from the electromotive-force data of Harned and Cook [48]. For molalities of potassium chloride from 0 to 0.2, $-\log \sqrt{a_w}$ is 0.0072 m. The nonelectrolyte, ammonia, is presumed to have a much smaller effect on the activity of water in these buffer solutions than does the ionized ammonium chloride. Furthermore, the water activity departs so slightly from unity that it can be considered, for the purpose at hand, equal to that in a solution of potassium chloride of the same molality. The values of $\sqrt{a_w/f_{NH_3}}$ given in the second column of table 9 were accordingly evaluated from the activity coefficient of ammonia found by Matthews and Davies and from the activity of water in solutions of potassium chloride,

as given by Stokes. The mean ionic activity coefficient of ammonium chloride in these equimolal buffer solutions at 25° C, derived from $\sqrt{a_w}/f_{NH_3}$ and the data of table 8, is given in the third column.

The activity coefficients of ammonium chloride in its pure aqueous solution at the freezing point were determined by Scatchard and Prentiss [32]. In order to make a comparison at 25° C, these values have been corrected from 0° to 25°. It was assumed for the computation that $\overline{L}_2$, the relative partial molal heat content of ammonium chloride, is constant for each concentration in this range of temperature and equal to that listed in the last column of table 9 [6, 49]. Inasmuch as $\log (\sqrt{a_w}/f_{NH_3})$ is so nearly zero, $d \log (\sqrt{a_w}/f_{NH_3})/dT$ is probably also small and, hence, as an approximation,

$$\overline{L}_2 \approx 4.6052 \, RT^2 \left[\frac{d(-\log f_\pm)}{dT} \right]. \qquad (27)$$

The values of $\overline{L}_2$, the relative partial molal heat content of ammonium chloride in the buffer solutions, were computed by eq 27 and are listed in the fifth column of table 9.

TABLE 9. *Mean ionic activity coefficient, $f_\pm$, and relative partial molal heat content $\overline{L}_2$, of ammonium chloride in equimolal buffer solutions compared with corresponding values in pure aqueous solutions of the salt at 25° C*

m	$\sqrt{a_w}/f_{NH_3}$	$f_\pm$ in—		$\overline{L}_2$ in—	
		Buffer	Water	Buffer	Water
				cal	cal
0.005	1.000	0.925	0.908	49	42
.01	1.001	.898	.877	65	56
.02	1.001	.864	.841	89	72
.05	0.998	.810	.784	138	98
.07	.997	.788	--------	155	109
.1	.995	.764	.735	179	121

The difference between $\overline{L}_2$ for ammonium chloride in water and in an aqueous solution of ammonia are not large. The activity coefficient in the buffer solution appears to be somewhat greater than in the pure aqueous solution. This difference, except for the part that can be attributed to errors in the two determinations, is a measure of the medium effect of ammonia upon the activity coefficient of ammonium chloride. However, the observed increase at 0.1 m is about three times as great as the medium effect of 0.1–M acetic acid upon the activity coefficient of 0.1–M hydrochloric acid [50].

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