The total volume of solution containing 1000 g. of water may be obtained by integrating $\bar{V}_2$ with respect to m. The result is

$$V = \left(\frac{1000}{d_1}\right) + \phi^\circ m + am^{3/2} + bm^2 + cm^{5/2} \quad (4)$$

If the integration constant, which represents the volume of 1000 g. of pure water at the given temperature, is obtained by inserting experimental values into equation 4, values are obtained which are practically coincidental with the experimental volumes of pure water at the same temperatures.

Finally, the partial molal volume of the water may be obtained as a function of the molality by utilizing the expression

$$\bar{V}_1 = \left(\frac{18.016}{d_1}\right) - 0.018016\,[1/2\,am^{3/2} + bm + 3/2\,cm^{5/2}] \quad (5)$$

The intercepts represent the molal volume of pure water at the given temperatures. The partial molal volumes of water are also plotted in Fig. 2.

The maxima and minima in the curves of $\bar{V}_2$ and $\bar{V}_1$ in Fig. 2 occur at approximately $m = 13.2$. This concentration corresponds to 4.2 moles of water per mole of calcium nitrate. This ratio is of doubtful significance because there does not appear to be any sharp break in the curve. These stationary points may indicate, however, a change in the status of hydration of the solute or of molecular association of the solvent or solute.

Summary

The densities of aqueous solutions of calcium nitrate have been determined over the concentration range one to twenty molal, and the temperature range 25 to 60°. The solutions were supersaturated in a part of these ranges.

Analytical expressions for the partial molal volumes of both the solute and solvent, the apparent molal volume of the solute, and the total volume of solution, as a function of $\sqrt{m}$, have been determined.

A maximum in the partial molal volume of calcium nitrate and a minimum in the partial molal volume of water have been observed.

BETHLEHEM, PENNSYLVANIA RECEIVED JULY 27, 1949

[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS]

Dissociation Constant of Aqueous Ammonia at 0 to 50° from E. m. f. Studies of the Ammonium Salt of a Weak Acid

BY ROGER G. BATES AND GLADYS D. PINCHING

The acidic dissociation constant of ammonium ion has been determined recently from measurements of the electromotive force of cells with hydrogen electrodes and silver–silver chloride electrodes in buffer–chloride solutions[1] by the method that has proved successful in studies of the ionization of many weak acids and ampholytes.[2] However, this procedure is not ideally suited to investigations of basic dissociation. For highest accuracy, corrections for the solubility of silver chloride in the cell solutions and for volatility of the free base may be necessary. It is nonetheless desirable that the dissociation constants of bases should relate to the hydrogen–silver chloride cell. If the ratio of the concentration of base to that of salt is small, the corrections may be insignificant, but the exact buffer ratio is still difficult to establish. Hence, in some instances the constant can be obtained to better advantage from electromotive force measurements of the hydrolysis of a salt of the weak base with a weak acid of known dissociation constant.[3] If the constant, K_a, of the acid selected is appreciably greater than K_w/K_b (the ratio of the ionization constant of water to the dissociation constant of the base), the concentration of free base formed by hydrolysis may be small. In contrast with the conventional method, the buffer ratio need not be known precisely. Furthermore, the combined buffer action of the two systems assures an adequate buffer capacity, even though the degree of hydrolysis be rather small.

When the base is uncharged and the acid is a singly charged anion, the extrapolation to zero ionic strength is made with somewhat more certainty than in the usual method. However, the precision in K_b obtainable is only one-half that of the conventional procedure, for, in addition to ionic concentrations, the electromotive force is dependent upon the geometric mean of K_a and K_w/K_b rather than upon K_w/K_b alone. This method can be employed successfully only when log K_a and log (K_w/K_b) differ by less than 2 units. Thus ammonium acetate and secondary ammonium phosphate (or microcosmic salt, $NaNH_4HPO_4 \cdot 4H_2O$) are insufficiently hydrolyzed to yield accurate results. The dissociation constant of ammonia at 0 to 50° has now been calculated from electromotive force studies of the extent of hydrolysis in mixtures of ammonia and potassium *p*-phenolsulfonate. The results are in good agreement with the earlier determination.[1]

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[1] R. G. Bates and G. D. Pinching, *J. Research Natl. Bur. Standards*, **42**, 419 (1949).

[2] (a) H. S. Harned and R. W. Ehlers, THIS JOURNAL, **54**, 1350 (1932); (b) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Chapter 15, Reinhold Publishing Corp., New York, N. Y., 1943.

[3] R. G. Bates and G. D. Pinching, *J. Research Natl. Bur. Standards*, **43**, 519 (1949).

TABLE I

*pw*H OF MIXTURES OF AMMONIA, POTASSIUM *p*-PHENOLSULFONATE AND POTASSIUM CHLORIDE, EACH OF MOLALITY *m*

m	*pw*H at										
	0°	5°	10°	15°	20°	25°	30°	40°	40°	45°	50°
0.10367	9.7950	9.6726	9.5522	9.4371	9.3264	9.2193	9.1199	9.0229	8.9294	8.8424	8.7587
.10188	9.7978	9.6735	9.5524	9.4366	9.3265	9.2199	9.1192	9.0231	8.9308	8.8443	8.7600
.09118	9.7923	9.6677	9.5470	9.4318	9.3213	9.2148	9.1149	9.0186	8.9256	8.8389	8.7542
.07878	9.7865	9.6618	9.5415	9.4269	9.3164	9.2099	9.1094	9.0135	8.9196	8.8321	8.7492
.06123	9.7773	9.6532	9.5327	9.4183	9.3081	9.2029	9.1022	9.0068	8.9145	8.8283	8.7441
.05179	9.7691	9.6451	9.5255	9.4116	9.3014	9.1970	9.0959	8.9999	8.9077	8.8216	8.7382
.04167	9.7646	9.6403	9.5203	9.4068	9.2970	9.1922	9.0920	8.9975	9.9048	8.8186	8.7347
.02608	9.7518	9.6280	9.5089	9.3951	9.2854	9.1824	9.0810	8.9858	8.8913	8.8049	8.7237
.017230	....	9.6198	9.5026	9.3899	9.2801	9.1747	9.0754	8.9799	8.8882	8.8020	8.7181
.010687	9.7333	9.6112	9.4930	9.3796	9.2701	9.1659	9.0655	8.9694	8.8779	8.7922	8.7080

Experimental

Ammonia solutions, about 0.1 *M*, were prepared by absorption of ammonia gas in deaerated conductivity water contained in a paraffin-lined flask. A stream of nitrogen removed the gas from a concentrated solution contained in a gas-washing bottle and conducted it into the flask. The concentration of ammonia was determined by weight titration with a 0.1 *M* solution of distilled hydrochloric acid, the chloride concentration of which had been determined gravimetrically. The indicator was methyl red, and a color standard was used in establishing the end-point. Potassium *p*-phenolsulfonate was decolorized with activated charcoal and then subjected to four crystallizations, the last one from conductivity water. The salt was dried at 90 to 110°. The potassium chloride was a fused sample from which bromide had been removed.[4]

The cell vessels have been described.[1] A stopcock, open only at the time of measurement, separated the electrode compartments. It was lubricated with a thin film of "high-vacuum" silicone grease. The hydrogen passed through a triple saturator containing cell solution before entering the electrode compartment. Temperature measurements were made with a platinum resistance thermometer.

Results

In Table I are listed *pw*H values for 10 equimolal mixtures of ammonia, potassium phenolsulfonate and potassium chloride. These were computed from the electromotive force, *E*, of the cell

Pt; H_2 (1 atm), NH_3 (*m*), KH Phenolsulfonate (*m*), AgCl; Ag

by the formula

$$pw\text{H} \equiv -\log(f_H f_{Cl} m_H) = \frac{(E - E^\circ)\mathbf{F}}{2.3026\,RT} + \log m_{Cl} \qquad (1)$$

where *m* is molality and *f* is an activity coefficient on the molal scale, and the other symbols have their customary meaning.[5] The *pw*H is a useful unit of acidity defined uniquely by equation (1).[6] On the other hand, a calculation of the *p*H ($-\log f_H m_H$) rests upon the arbitrary evaluation of an individual ionic activity coefficient.[7] The *pw*H is formally related to *p*H by

$$pw\text{H} = p\text{H} - \log f_{Cl} \qquad (2)$$

and becomes equal to it at zero concentration.

Calculation of Dissociation Constants

The hydrolysis of potassium ammonium *p*-phenolsulfonate (KNH_4Ps) can be represented by

$$NH_4^+ + Ps^= + 2H_2O = NH_3 + HPs^- + H_3O^+ + OH^- \qquad (3)$$

The equilibrium constant for (3) is K_w^2/K_aK_b or K_wK_{bh}/K_a, where K_{bh} is the constant for the acidic dissociation of ammonium ion, $NH_4^+ + H_2O = NH_3 + H_3O^+$, and K_b is the constant for the basic of dissociation of ammonia, $NH_3 + H_2O = NH_4^+ + OH^-$. As a first approximation, the *pw*H of a solution of such a salt lies midway between pK_a and pK_{bh} and is nearly independent of concentration. Since pK_a and pK_{bh} are both about 9, it is clear that the ions of the salt hydrolyze to different extents. Indeed it is incorrect in general to speak of the degree of hydrolysis of a salt of a weak acid and weak base. If α_1 and α_2 are the degrees of hydrolysis of NH_4^+ and $Ps^=$, respectively, the complete expression for $^1/_2\,(pK_{bh} + pK_a)$ can be written by combining (1) with the mass-law expressions for the acidic dissociations of NH_4^+ and HPs^-

$$^1/_2(pK_{bh} + pK_a) = pw\text{H} + {^1/_2}\log\frac{\alpha_2(1-\alpha_1)}{\alpha_1(1-\alpha_2)} + {^1/_2}\log\frac{f_{NH_4^+}f_{HPs^-}f^2_{Cl^-}}{f_{NH_3}f_{Ps^=}} \qquad (4)$$

The second term on the right of (4) is small when *m* exceeds 0.01, α_2 is greater than 0.1, and the *p*H lies between 4 and 10. For the most dilute solution studied here, this term amounted to 0.0023 at 50° and to 0.0007 at 0°. Hence, it was permissible to compute, by the Debye–Hückel formula,[8] the activity coefficients needed in its evaluation and to make other approximations as necessary. As the dissociation constant of the acid is known, we have from the mass law

$$\log\frac{1-\alpha_2}{\alpha_2} \approx pw\text{H} - pK_a + \frac{2A\sqrt{\mu}}{1 + 8B\sqrt{\mu}} \qquad (5)$$

where μ is the ionic strength and *A* and *B* are constants of the Debye–Hückel equation.[9] The value of 8 for the ion-size parameter in equation (5) was obtained from earlier studies of phenolsulfo-

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(4) G. D. Pinching and R. G. Bates, *J. Research Natl. Bur. Standards*, **37**, 311 (1946).

(5) Values of E° and 2.3026 $RT/\mathbf{F}$ in absolute volts are summarized in ref. 1.

(6) E. A. Guggenheim, *J. Phys. Chem.*, **34**, 1758 (1930); D. I. Hitchcock, THIS JOURNAL, **58**, 855 (1936).

(7) R. G. Bates, *Chem. Revs.*, **42**, 1 (1948).

(8) P. Debye and E. Hückel, *Physik. Z.*, **24**, 185 (1923).

(9) G. G. Manov, R. G. Bates, W. J. Hamer and S. F. Acree, THIS JOURNAL, **65**, 1765 (1943).

nate buffer systems.[10] The solutions are alkaline, and m_{OH} represents closely the difference between the concentration of phenolsulfonate ion produced by hydrolysis and that of the ammonia produced. Hence

$$\alpha_2 - \alpha_1 \approx m_{OH}/m \qquad (6)$$

Furthermore, if the activity coefficients of chloride and hydroxyl ions are equal

$$-\log m_{OH} = pK_w - pwH \qquad (7)$$

The α term of (4) was computed from the experimental data by equations (5), (6) and (7). The ionic strength of the solutions is

$$\mu = 4m - {}^1/_2 m(3\alpha_2 + \alpha_1) + {}^1/_2(m_H + m_{OH}) \approx 4m(1 - \alpha_2/2) \qquad (8)$$

To facilitate the extrapolation to zero ionic strength, the last term of (4) was expressed as before[3] in terms of two ion-size parameters, a_1 and a_2, characteristic of the ammonia and phenolsulfonate buffer systems, respectively. A satisfactory linear extrapolation at each temperature was provided by $a_1 = 4$ and $a_2 = 10$. Hence

$$ {}^1/_2\log \frac{f_{NH_4^+} f_{Ps^-} f^2_{Cl}}{f_{NH_3} f_{Ps^=}} + \beta'\mu = \frac{-6AB\mu}{(1 + 7B\sqrt{\mu})^2} \qquad (9)$$

where -6 is $a_1 - a_2$ and 7 is $(a_1 + a_2)/2$. The "apparent" ${}^1/_2$ $(pK_{bh} + pK_a)$ computed by replacement of the last term of (4) by the right side of equation (9) gave a straight line of slope β' when plotted as a function of μ as shown in Fig. 1. This apparent value is designated ${}^1/_2(pK_{bh} + pK_a)'$. The dotted line was calculated by using $4B$ instead of $8B$ as the coefficient of the $\sqrt{\mu}$ term in the denominator of (5). Evidently the final result is unchanged.

Discussion

The slopes, β', of the extrapolation lines were determined and $\beta'\mu$ subtracted from each value of ${}^1/_2(pK_{bh} + pK_a)'$ in order that the average values listed in Table II could be computed. The third column lists pK_{bh} obtained by combining the results in the second column with pK_a for p-phenolsulfonate ion at the 11 temperatures.[10] For comparison, the value of pK_{bh} reported earlier[1] is given in the fourth column. In the fifth column pK_b, the negative logarithm of the basic dissociation constant of ammonia obtained by subtracting pK_{bh} from pK_w[2b] is listed. The values of K_b are given in the last column.

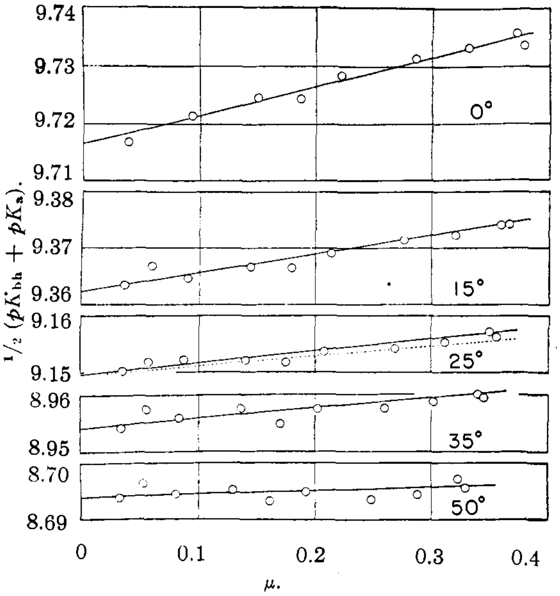

Fig. 1.—Determination of ${}^1/_2$ $(pK_{bh} + pK_a)$.

TABLE II

SUMMARY OF THE DISSOCIATION CONSTANTS FOR AMMONIA AND AMMONIUM ION

t	${}^1/_2(pK_{bh} + pK_a)$	pK_{bh}	pK_{bh} (Ref. 1)	pK_b	$K_b \times 10^5$
0	9.7163 ± 0.0009	10.081	10.081	4.862	1.374
5	9.5933 ± 0.0005	9.903	9.904	4.830	1.479
10	9.4749 ± 0.0006	9.730	9.731	4.804	1.570
15	9.3621 ± 0.0006	9.564	9.564	4.782	1.652
20	9.2531 ± 0.0006	9.401	9.400	4.767	1.710
25	9.1494 ± 0.0006	9.246	9.245	4.751	1.774
30	9.0489 ± 0.0007	9.093	9.093	4.740	1.820
35	8.9540 ± 0.0009	8.947	8.947	4.733	1.849
40	8.8628 ± 0.0014	8.805	8.805	4.730	1.862
45	8.7770 ± 0.0013	8.671	8.670	4.726	1.879
50	8.6939 ± 0.0009	8.540	8.539	4.723	1.892

In the earlier work,[1] corrections to pwH of 0.002 to 0.003 for the solubility of silver chloride in the equimolal mixtures of ammonia and ammonium chloride were necessary. In the present investigation, α_2 reached 0.5 in the most dilute solution at 50°. Nevertheless, the correction for solubility amounted to only 0.0004 in pwH, for the molality of chloride was twice that of the ammonia.

The agreement between the two determinations of the acidic dissociation constant of ammonium ion is very satisfactory, inasmuch as the newer values reflect the combined errors in ${}^1/_2(pK_{bh} + pK_a)$ and in pK_a. At 25°, the basic dissociation constant of ammonia, K_b, was found to be 1.77×10^{-5}. The electromotive force measurements of Owen[11] with the silver–silver iodide electrode gave 1.75×10^{-5}. Everett and Wynne-Jones[12] found a lower value, namely, 1.65×10^{-5}, by another e. m. f. method. Nevertheless, the molal enthalpy and entropy changes for the dissociation process derived from their dissociation constants in the range 5 to 45° agree well with those obtained from the data in Table II.[1] Conductance measurements furnish a value of about 1.82×10^{-5} for K_b at 25°.[13]

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[10] R. G. Bates, G. L. Siegel and S. F. Acree, *J. Research Natl. Bur. Standards*, **31**, 205 (1943); R. G. Bates, P. T. Diamond, M. Eden and S. F. Acree, *ibid.*, **37**, 251 (1946).

[11] B. B. Owen, THIS JOURNAL, **56**, 2785 (1934).

[12] D. H. Everett and W. F. K. Wynne-Jones, *Proc. Roy. Soc. (London)*, **169A**, 190 (1938); *Trans. Faraday Soc.*, **35**, 1380 (1939).

[13] A. A. Noyes, Y. Kato and R. B. Sosman, *Z. physik. Chem.*, **73**, 1 (1910); G. N. Lewis and P. W. Schutz, THIS JOURNAL, **56**, 1913 (1934).

Summary

The dissociation constant of ammonia has been determined at intervals of 5° from 0 to 50° by electromotive force measurements of the extent of hydrolysis of the salt formed from ammonia and the weak acid potassium *p*-phenolsulfonate. The results were in good agreement with those obtained previously by another electromotive force method.

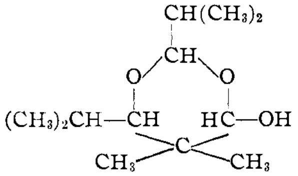
WASHINGTON, D. C. RECEIVED AUGUST 15, 1949

NOTES

The Trimer of Isobutyraldehyde

BY ELLIOT R. ALEXANDER AND ELLIOT N. MARVELL[1]

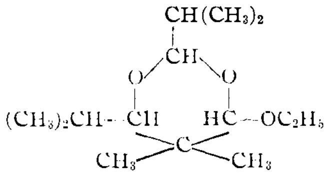
In an earlier communication,[2] Saunders, Murray and Cleveland have pointed out that Raman spectra indicate the formula I for the trimer of



I

isobutyraldehyde which is usually obtained by attempted aldolization. We have obtained additional chemical evidence in support of this formulation.

When the pure trimer was treated with ethyl orthoformate, a homogeneous product was obtained in good yield which did not react with metallic sodium and which did not discolor potassium permanganate or bromine in carbon tetrachloride solution. On long standing the liquid produced a weak color with a Fuchsin reagent but it gave negative tests with Fehling or Tollens solutions. Infrared analysis indicated that oxygen was present only in the form of ether linkages. These data, together with the correct analysis for carbon, hydrogen, ethoxyl groups, molecular weight and molecular refractivity, are in agreement with the formula II for our product.



II

Experimental[3]

Reaction of the Trimer of Isobutyraldehyde with Ethyl Orthoformate.—By the procedure used for the reaction of hydroxypivaldehyde with ethyl orthoformate,[4] 48.1 g. (0.222 mole) of the trimer of isobutyraldehyde[1] (b.p. 80° (1.0 mm.); n^{20}_{D} 1.4487) was treated with 45.0 g. (0.31 mole) of ethyl orthoformate. After distillation through an eight inch electrically heated column packed with glass helices, the product (42.0 g., 78%) was obtained as a homogeneous colorless liquid, b.p. 61° (1.5 mm.); n^{20}_{D} 1.4321; d^{20}_{20} 0.9162. This material did not react with metallic sodium, potassium permanganate or bromine in carbon tetrachloride solution. Fehling and Tollens tests were also negative. On long standing, the liquid produced a weak color with fuchsin reagent. Infrared analysis indicated that oxygen was present only in the form of ether linkages.[5] These properties are those to be expected of 2,4-diisopropyl-5,5-dimethyl-6-ethoxy-1,3-dioxane (II).

Anal.[6] Calcd. for $C_{14}H_{28}O_3$: C, 68.82; H, 11.53; ethoxyl, 18.40; mol. wt., 244; M^{20}_{D}, 69.60. Found: C, 68.97; H, 11.56; ethoxyl, 18.59; mol. wt., 238; M^{20}_{D}, 69.23.

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(1) Present address: Oregon State College, Corvallis, Oregon.

(2) Saunders, Murray and Cleveland, THIS JOURNAL, **65**, 1714 (1943).

(3) All melting points and boiling points are uncorrected.

(4) Alexander and Marvell, THIS JOURNAL, **71**, 15 (1949).

(5) We are indebted to Dr. Foil A. Miller and Mrs. J. L. Johnson for the determination and interpretation of these spectra.

(6) The microanalyses were performed by Miss Theta Spoor and the Howard Clark Microanalytical Laboratories, Urbana, Illinois.

DEPARTMENT OF CHEMISTRY
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Preparation of N-Acetyl-DL-amino Acids

BY NOEL F. ALBERTSON

It has been shown that acid hydrolysis of an alkylacetamidomalonic ester gives the amino acid as the end-product of the reaction, whereas hydrolysis with excess sodium hydroxide leads to the formation of the sodium salt of the alkylacetamidomalonic acid.[1,2] In the case of alkylacetamidocyanoacetic ester the end-product is the amino acid with either acid or caustic hydrolysis.[2,3] It has now been found that hydrolysis of an alkylacetamidomalonic ester with aqueous sodium carbonate leads directly to the sodium salt of the acetyl-DL-amino acid. The same results are obtained with the alkylacetamidocyanoacetic esters although the reaction time is longer. The method should prove generally useful for the preparation of N-acetyl-DL-amino acids. This procedure also affords a means of degrading alkylacetamidoma-

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(1) Snyder and Smith, THIS JOURNAL, **66**, 350 (1944).

(2) Albertson, *ibid.*, **68**, 450 (1946).

(3) Albertson and Tullar, *ibid.*, **67**, 502 (1945).