[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

THE THERMODYNAMIC PROPERTIES OF WEAK ACIDS AND BASES IN SALT SOLUTIONS, AND AN EXACT METHOD OF DETERMINING THEIR DISSOCIATION CONSTANTS[1]

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Recently, Harned and Robinson[2] showed that it is possible to determine the hydrogen-ion concentration and activity coefficient of acetic acid in chloride solutions of various kinds and strengths from measurements of the electromotive forces of cells without liquid junctions. To make their calculations, the dissociation constant of acetic acid determined by conductance measurements was employed. In the present study it will be shown that an exact evaluation of the dissociation constant may be obtained from the cell measurements alone. To demonstrate the method, we shall first employ Harned and Robinson's data relating to acetic acid in sodium chloride solutions, and then present some more accurate results on formic acid in sodium chloride solutions. Finally, we shall apply the method to some weak bases by computing the dissociation constants of ammonia and some methylamines from Harned and Robinson's data. These latter will not be so exact as in the case of the acids because of an approximation introduced into the calculation, and because of the special kind of liquid junction used in the cells containing the weak hydroxides.

Since the dissociation constant of a weak electrolyte has usually been determined by the conductance method, or by electrometric methods which involve liquid junction potentials, it is a matter of considerable importance to devise a method which rests entirely upon an exact thermodynamic basis.

Outline of the Method.—Let E represent the electromotive forces of the cells

$$H_2/HAc(M),\ NaCl\ (m)/AgCl/Ag$$

and 0.4644 the electromotive force of the cell

$$H_2/HCl(0.01)/AgCl/Ag$$

Then the electromotive force of the cell

$$H_2/HAc(M),\ NaCl(m)/AgCl/Ag/AgCl/HCl(0.01)/H_2$$

will be given by

$$E-0.4644 = 0.05915 \log \frac{(0.904)^2\,(0.01)^2}{(\gamma_{HCl})^2\, m_H m}\text{, or}$$

$$16.9062\,E-3.7636 + \log m + 2 \log \gamma_{HCl} = -\log m_H \tag{1}$$

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[1] This paper represents a part of the thesis presented by Benton B. Owen to the Graduate School of Yale University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Harned and Robinson, THIS JOURNAL, **50**, 3157 (1928).

if we take the activity coefficient of hydrochloric acid to be 0.904[3] at 0.01 molal concentration. γ_{HCl} is the activity coefficient of hydrochloric acid in the solution containing the undissociated acetic acid molecule at a molal concentration of $(M - m_H)$. When M is zero, γ_{HCl} becomes the activity coefficient of hydrochloric acid in pure, aqueous, sodium chloride solutions, and will be denoted $\overset{\circ}{\gamma}_{HCl}$. The values of E for the weak acid–sodium chloride cells, and 0.4644 for the reference cell were obtained under identical experimental conditions, so that the double cell indicated does not include any experimental inconsistencies. It should also be remarked that our final results are independent of the choice of 0.904 as the activity coefficient of 0.01 M HCl. In Equation 1, as first written, the term γ_{HCl} is referred to 0.904 and enters the calculations only in a ratio with this reference value. Thus, at the start, the present method is considerably more advantageous than that employed by Cohn[4] and others in which their choice of this reference value influences the final values by several per cent. From Equation 1 we may write the identity

$$16.9062\,E - 3.7636 + \log m + 2 \log \gamma^{\circ}_{HCl} = -\log m_H - 2 \log \frac{\gamma_{HCl}}{\gamma^{\circ}_{HCl}} \qquad (2)$$

This is Equation 14a in Harned and Robinson's paper.[2] Since $\overset{\circ}{\gamma}_{HCl}$ and not γ_{HCl} is known in salt solutions, our first step will be to drop the term containing γ_{HCl} in Equation 2, and define an unreal hydrogen-ion concentration, m'_H, by means of the equation

$$16.9062\,E - 3.7636 + \log m + 2 \log \gamma^{\circ}_{HCl} = -\log m'_H \qquad (3)$$

m'_H would be the true hydrogen-ion concentration if $\overset{\circ}{\gamma}_{HCl}$ was not changed to γ_{HCl} by the variation of the character of the medium caused by the addition of the undissociated molecule of the weak acid, HA. Since the activity coefficient of hydrochloric acid relative to unity at infinite dilution in water is affected considerably by this variation of the medium, the quantity m'_H will be designated throughout the following discussion as the "apparent hydrogen-ion concentration," which will serve to differentiate it from the true hydrogen-ion concentration. Later when we come to learn more of the effect of the medium on both m'_H and γ_{HCl}, we shall show how the true hydrogen-ion concentration may in all cases be computed.

By subtracting (3) from (2), we obtain

$$\log \frac{m'_H}{m_H} = 2 \log \frac{\gamma_{HCl}}{\gamma^{\circ}_{HCl}} \qquad (4)$$

which relates the true and apparent hydrogen-ion concentrations. Harned and Robinson estimated approximately the right-hand member of Equation 4 by assuming that the variation of γ_{HCl} with M was the same for

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[3] Randall and Young, This Journal, **50**, 989 (1928).

[4] Cohn, *ibid.*, **50**, 696 (1928).

water–acetic acid mixtures as for water–alcohol mixtures. As a part of this investigation it will be shown that this quantity may be determined accurately from the electromotive forces of the acetic acid–sodium chloride cells.

The thermodynamic equation for the dissociation of the acid is

$$K = \frac{\gamma_{H}\gamma_{Ac}m_{H}m_{Ac}}{\gamma_{HAc}m_{HAc}} = \gamma_{A}^{2}\frac{m_{H}^{2}}{M - m_{H}} = \gamma_{A}^{2}\, k \tag{5}$$

This equation is valid when γ_A equals unity at infinite dilution of electrolyte in a given solvent. Thus, k approaches K as the ionic strength becomes zero. Since our first computation yields the apparent hydrogen-ion concentration, m'_{H}, and not m_H, we must employ another set of quantities defined by

$$K = \frac{\gamma'_{H}\gamma'_{Ac}m'_{H}m'_{Ac}}{\gamma'_{HAc}m'_{HAc}} = \gamma'^{2}_{A}\frac{m'^{2}_{H}}{M - m'_{H}} = \gamma'^{2}_{A}\, k' \tag{6}$$

The primed quantities in this equation are all apparent values because of their relation with m'_{H}. Further, k' does not approach K as the ionic strength approaches zero nor does γ'_{A} approach unity under this condition. Consequently, the limiting value of these functions will be written k° and $\overset{\circ}{\gamma}_{A}$. As a result we may write

$$K = \gamma_{A}^{2}k = \gamma'^{2}_{A}k' = \overset{\circ}{\gamma}{}^{2}_{A}k^{\circ} \tag{7}$$

It should be noted here that γ_A corresponds to $\gamma_{(\text{corr.})}$, the corrected activity coefficient, and γ'_{A} to γ_A in Harned and Robinson's paper.

The Extrapolation of k' to Infinite Dilution of Both Ions and Undissociated Acetic Acid Molecules.—If we take the logarithm of Equation 5, we obtain

$$\log K = 2 \log \gamma_{A} + \log k \tag{8}$$

For moderate concentrations, the activity coefficient of any uni-univalent electrolyte, referred to unity at infinite dilution in a given solvent, may be expressed as a function of the ionic strength by the semi-empirical equation

$$2 \log \gamma_{A} = -A\sqrt{\mu} + 2B\mu \tag{9}$$

The constant A is equal to unity for aqueous solutions, whence it will suffice for our purpose to combine Equations 8 and 9 to give

$$\log k - \sqrt{\mu} = \log K - 2B\mu \tag{10}$$

Thus, if we plot $(\log k - \sqrt{\mu})$ against μ, a straight line should be obtained, and the intercept for $\mu = 0$ will be $\log K$. Several investigators[5] have employed Equation 10 as a basis for similar extrapolations, but, as we have pointed out before, k' and not k is directly measurable. Furthermore, since m'_{H} and not m_H is used in calculating the ionic strength, the latter must be written μ' and not μ. In salt solutions of weak acids the

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[5] Bjerrum and Unmack, *Det. Kgl. Danske Videnskab. Selskab. Math.-fys. Medd.*, **9**, 1 (1929); Sihvonen, *Z. Electrochem.*, **36**, 165 (1930).

difference between μ' and μ is very small and does not alter the plot appreciably. In practice, therefore ($\log k' - \sqrt{\mu'}$) is plotted against μ', and although this plot is a straight line, the intercept is not $\log K$, but is a quantity which we shall denote $\log k°$. From the definition of k and k', and Equation 7, we may write

$$\log \frac{k'}{k} = 2 \log \frac{\gamma_A}{\gamma'_A} = 2 \log \frac{m'_H}{m_H} - \log \frac{M - m'_H}{M - m_H} \tag{11}$$

Since for acids of the strength of acetic the last term on the right is less

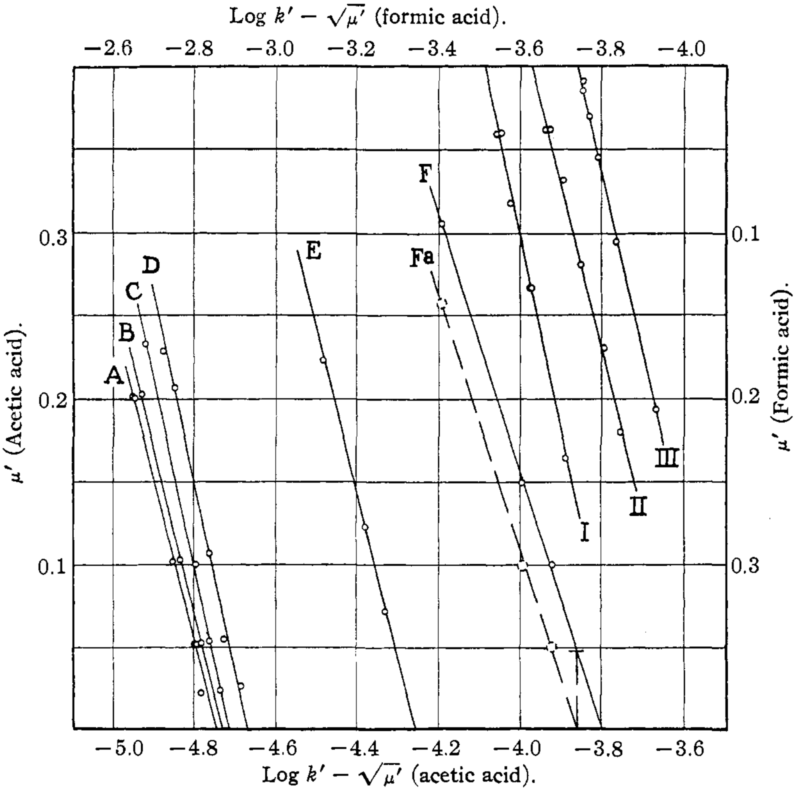

Fig. 1.—Acetic and formic acids in sodium chloride solutions. Molality of acetic acid: A, 0.1; B, 0.2; C, 0.52; D, 1.0; E, 5.41; F, 10.2. Molality of formic acid: I, 2.13; II, 1.0; III, 0.1.

than 0.0008 when M equals 5, it may be neglected. Consequently, rewriting Equation 11 and introducing Equation 4, we obtain

$$\log \frac{k'}{k} = 2 \log \frac{\gamma_A}{\gamma'_A} = 2 \log \frac{m'_H}{m_H} = 4 \log \frac{\gamma_{HCl}}{\gamma^{\circ}_{HCl}} \tag{12}$$

Further, by combining this equation with (7) and (10), we obtain

$$\log k' - \sqrt{\mu} = \left((\log k^{\circ} + 2 \log \gamma^{\circ}_A + 4 \log \frac{\gamma_{HCl}}{\gamma^{\circ}_{HCl}}\right) - 2B\,\mu \tag{13}$$

At zero ionic strength, 2 log (γ_A/γ'_A) becomes 2 log $1/\gamma_A^\circ$ by definition, whence by Equation 12

$$2 \log \gamma_A^\circ + 4 \log \frac{\gamma_{HCl}}{\gamma_{HCl}^\circ} = 0, \text{ when } \mu = 0 \tag{14}$$

Consequently, the bracketed member on the right of Equation 13 is log k°.

Since μ' may be written for μ without appreciable error, Equation 13 becomes

$$\log k' - \sqrt{\mu'} = \log k^\circ - 2B\,\mu' \tag{15}$$

Figure 1 shows the plot of $(\log k' - \sqrt{\mu'})$ against μ' for various concentrations of acetic acid in sodium chloride solutions which has been drawn by the use of the data contained in Table I and from which it is obvious that straight lines are obtained.

Table I

The Apparent Hydrogen-Ion Concentrations of Acetic Acid in Sodium Chloride Solutions

M	m	$2 \log \gamma_{HCl}^\circ$	m'_H	$\log k' - \sqrt{\mu'}$	μ'
0.10	0.0	....	0.0	(−4.7438)	0.0
.0997	.02	$\bar{1}.8790$	.001506	−4.7830	.0215
.0992	.05	$\bar{1}.8306$	.001617	−4.7992	.0516
.1003	.05	$\bar{1}.8306$	.001634	−4.7940	.0516
.0991	.1	$\bar{1}.7906$	.001692	−4.8509	.1017
.1004	.1985	$\bar{1}.7552$	.001764	−4.9483	.2003
.0991	.2	$\bar{1}.7545$	.001741	−4.9562	.2017
.20	.0	....	.0	(−4.7308)	.0
.1965	.05	$\bar{1}.8300$	.002335	−4.7806	.0523
.2018	.1	$\bar{1}.7900$	.002471	−4.8339	.1025
.2018	.2	$\bar{1}.7542$	.002570	−4.9294	.2026
.52	.0	....	.0	(−4.7156)	.0
.519	.02	$\bar{1}.8738$	.003675	−4.7359	.0238
.519	.05	$\bar{1}.8285$	.003901	−4.7614	.0539
.519	.0957	$\bar{1}.7918$	.004135	−4.7947	.0998
.519	.2285	$\bar{1}.7481$	.004337	−4.9197	.2328
1.00	.0	....	.0	(−4.6694)	.0
1.002	.01997	$\bar{1}.8702$	.005475	−4.6852	.0254
1.002	.049	$\bar{1}.8324$	.005666	−4.7256	.0547
1.002	.1	$\bar{1}.7882$	.006051	−5.7602	.1061
1.002	.2	$\bar{1}.7536$	.006352	−4.8466	.2064
1.002	.222	$\bar{1}.7488$	.006350	−4.8724	.2284
5.40	.0	....	.0	(−4.2552)	.0
5.41	.05	$\bar{1}.8114$	.02164	−4.3287	.0716
5.41	.1	$\bar{1}.7800$	.02245	−4.3793	.1225
5.39	.2	$\bar{1}.7500$	.02287	−4.4832	.2229
10.2	.0	....	.0	(−3.7970)	.0
10.2	.05	$\bar{1}.7914$	.05013	−3.9231	.1001
10.2	.0992	$\bar{1}.7692$	.04997	−3.9953	.1492
10.2	.257	$\bar{1}.7378$	.04825	−4.1921	.3053

The first two columns of the table are taken from Harned and Robinson's data. Column 3 contains the values of log $\overset{\circ}{\gamma}_{\mathrm{HCl}}$ at the same ionic strength as that obtaining in the acetic acid–sodium chloride cells. These values were obtained from a plot of log $\overset{\circ}{\gamma}_{\mathrm{HCl}}$[6] against $\sqrt{\mu}$ of the data given by Harned and Åkerlöf,[7] which have been recalculated to conform with the value 0.904 for 0.01 *M* hydrochloric acid in pure water. A trial value of $\overset{\circ}{\gamma}_{\mathrm{HCl}}$ was used to compute an approximate value of m'_{H}, which was then employed to compute a more exact value of μ by which a final value of log $\overset{\circ}{\gamma}_{\mathrm{HCl}}$ could be read from the plot. Column 4 contains the values of m'_{H}, calculated by Equation 3, and Columns 5 and 6 the corresponding values of the functions indicated. The quantities in parenthesis are the values of log $k°$ read from the plots in Fig. 1 for infinite dilution of ions. To obtain *K* it is now necessary to cross-extrapolate these values to infinite dilution of the acetic acid molecules. This can easily be accomplished since we find that $k°$ and *K* are related by

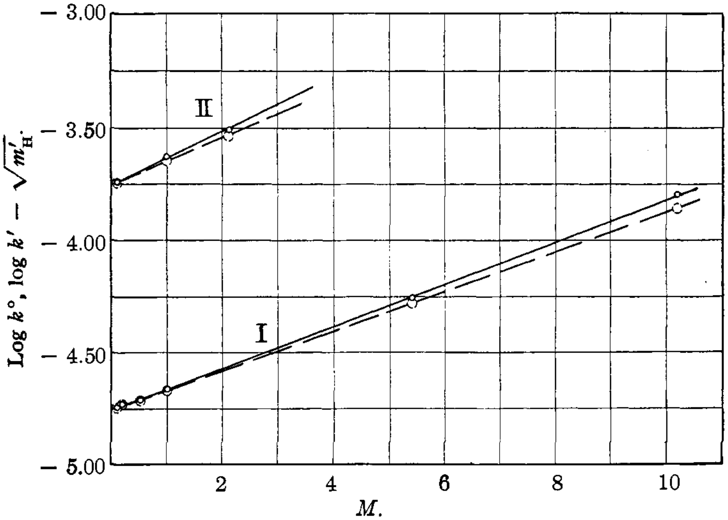

Fig. 2.—Extrapolation for log *K*. I, Acetic acid; II, formic acid. ——○——, log $k°$; — —○— —, log $k' - \sqrt{m'_{\mathrm{H}}}$.

$$\log \frac{k°}{K} = 2SM \qquad (16)$$

where *S* is an empirical constant which we shall call the medium effect, and *M* is molal concentration of the acetic acid. Figure 2 contains a plot

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[6] So long as m_{H} is of the order of 0.01 molal, or less, the values of the activity coefficient of hydrochloric acid in salt solutions are practically independent of m_{H} and depend only upon μ. Consequently, we have employed the 0.01 hydrochloric acid series throughout. This point was discussed in detail by Harned and Robinson.

[7] Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926).

of log k° against M. Since a straight line may be drawn through the points, Equation 16 is confirmed. From this plot we find that for acetic acid S equals 0.047 and log K equals -4.758, whence K equals 1.75×10^{-5} at 25°.

The Effect of Change of Solvent upon the Quantities under Consideration.—According to Equation 16, we found that log k°/K, the value of log (k'/k) extrapolated to zero ionic strength, varies linearly with the concentration of the weak acid. *If we make the important hypothesis that this effect of the medium due to the undissociated acid maintains at all ionic strengths or is independent of the electrolyte concentrations,* we may combine Equations 12 and 16 and obtain

$$2SM = \log \frac{k^\circ}{K} = 2 \log \frac{1}{\gamma_A^\circ} = \log \frac{k'}{k} = 2 \log \frac{\gamma_A}{\gamma_A'} = 2 \log \frac{m_H'}{m_H} = 4 \log \frac{\gamma_{HCl}}{\gamma_{HCl}^\circ} \quad (17)$$

From the parallel nature of the plots in Fig. 1 and the character of the results obtained by the application of this hypothesis, we regard it as a very close approximation. Upon the basis of this hypothesis, Equation 17 immediately allows the calculation of the true hydrogen-ion concentration and the true activity coefficient of acetic acid in sodium chloride solutions from the data in Table I. It also furnishes an evaluation of γ_{HCl}, the activity coefficient of hydrochloric acid in sodium chloride solutions containing undissociated molecules of acetic acid. Since Equation 17 summarizes the connection between the medium effect and all the thermodynamic quantities under consideration, we shall summarize the approximations involved. Reading from left to right, we shall consider each sign of equality in turn. The first equality is empirical and is justified by Fig. 2. The second is definitional and follows from Equation 7. The third involves the hypothesis that the medium effect is independent of the presence of ions. The fourth and sixth equalities are definitional, and the fifth involves neglecting the small term, log $(M-m_H')/(M-m_H)$, which, however, may be retained, as in Equation 11, if the accuracy of the data would seem to justify this complication.

Properties of the Salt-Free Acetic Acid Solutions, and an Alternate Extrapolation for K.—The dotted line, Fa, in Fig. 1 near that for 10.2 M acetic acid is the plot of $(\log k' - \sqrt{\mu'})$ against m, the sodium chloride concentration. If this is assumed to be straight, its intercept is nearly equal to $(\log k' - \sqrt{m_H'})$ for 10.2 acetic acid in pure water. A more exact value may be obtained from the equation

$$2 \log m_H' = R + \sqrt{m_H'} + \log (M - m_H') \quad (18)$$

in which R equals $(\log k' - \sqrt{m_H'})$. Approximate values of R and $m_H'(= \mu')$ are read from the plot, substituted in the right side of Equation 18 and solved for a more exact value of m_H', which in turn is used to read a more exact value of R from the plot. By repetition of this process until

Equation 18 is satisfied, exact values of R and m'_H may be obtained. These are given in Table II together with the true values of m_H and log γ_A calculated by Equation 17. The noticeable irregularity of these values of log γ_A is due to the fact that they represent the difference of two relatively large quantities and include the experimental discrepancy between the experimental points and the straight line in Fig. 2. Figure 2 also contains the plot of (log $k' - \sqrt{m'_H}$) against M, shown as large circles through which a straight line (dashed) extrapolates to log K. This value of K is almost exactly 1.75×10^{-5} and thus corresponds very closely to that obtained by means of the log $k°$, M plot.

TABLE II

THE APPARENT AND REAL HYDROGEN-ION CONCENTRATIONS OF M ACETIC ACID IN PURE WATER

M	R	m'_H	m_H	Log γ_A
0.0	(−4.7580)	0.0	0.0	0.0
.1	−4.7452	.001390	.001375	− .0204
.2	−4.7330	.002015	.001972	− .0256
.52	−4.7186	.003356	.003173	− .0243
1.0	−4.6740	.004985	.004474	− .0303
5.41	−4.2758	.01988	.01107	− .0574
10.2	−3.8600	.04820	.01598	− .0794

Measurements of Cells Containing Formic Acid in Sodium and Potassium Chloride Solutions at 25°.—The electrodes, cells and technique employed in these measurements were the same as described by Harned and Robinson. Table III contains the data. The significance of the various quantities is obvious from the previous discussion of acetic acid. Column 2 gives the observed electromotive force corrected to one atmosphere pressure of hydrogen and divided by 0.05915. All cells which attained equilibrium are included in the table. The electromotive forces of the entire 0.1 M formic acid series in potassium chloride and above 0.025 for m in the sodium chloride solutions are the means of duplicate cells. The average deviation of the individual values from the mean was about 0.04 millivolt for the latter and 0.09 for the former. The data for more concentrated formic acid solutions were obtained with somewhat less care since they were intended only to determine the value of the medium effect.

Figure 1 contains the plot of (log $k' - \sqrt{\mu'}$) against μ', and the extrapolated values of log $k°$ are given in parentheses in Table III, Column 5. The curve for 0.1 M formic acid in sodium chloride solutions, for which the highest accuracy is claimed, gives striking confirmation of the validity of Equation 15 up to $\mu' = 0.2$. The data for 0.1 M formic acid in potassium chloride solutions are not included in Fig. 1 since it extrapolates to the same value of log $k°$ as the corresponding sodium chloride curve,

TABLE III

THE APPARENT HYDROGEN-ION CONCENTRATION OF FORMIC ACID IN POTASSIUM AND SODIUM CHLORIDE SOLUTIONS

m	$\frac{E}{0.05915}$	2 Log $\gamma^{\circ}_{\mathrm{HCl}}$	m'_{H}	Log $k' - \sqrt{\mu'}$	m_{H}	Log γ_{A}
0.10031 Formic Acid, m Potassium Chloride						
	.....	....	0.0	(−3.7413)	0.0	0.0
0.05	7.53339	$\bar{1}.8228$	.005110	−3.7965	.005048	− .0897
.1	7.25630	$\bar{1}.7807$	.005329	−3.8489	.005264	− .1084
.2	6.97667	$\bar{1}.7398$	.005573	−3.9377	.005505	− .1285
.5	6.61420	$\bar{1}.7076$	.005531	−4.2021	.005464	− .1251
1.0	6.32291	$\bar{1}.7134$	.005337	−4.5257	.005274	− .1091
1.5	6.14505	$\bar{1}.7413$	.005026	−4.8034	.004965	− .0823
2.0	6.01369	$\bar{1}.7800$	.004666	−5.0587	.004609	− .0492
3.0	5.80423	$\bar{1}.8700$	.004095	−5.4918	.004046	.0088
0.10031 Formic Acid, m Sodium Chloride						
	.....	....	0.0	(−3.7413)	0.0	0.0
0.005	8.48690	$\bar{1}.9147$	.004603	−3.7530	.004547	− .0431
.01	8.19358	$\bar{1}.8966$	.004714	−3.7550	.004657	− .0538
.025	7.81234	$\bar{1}.8616$	.004918	−3.7689	.004858	− .0727
.05	7.52713	$\bar{1}.8269$	.005136	−3.7921	.005073	− .0920
.1	7.24277	$\bar{1}.7884$	.005401	−3.8370	.005336	− .1145
.2	6.95909	$\bar{1}.7537$	.005621	−3.9302	.005553	− .1323
.5	6.57346	$\bar{1}.7287$	.005788	−4.1617	.005717	− .1454
1.0	6.24937	$\bar{1}.7694$	.005558	−4.4896	.005490	− .1272
1.5	6.03686	$\bar{1}.8285$	.005275	−4.7604	.005211	− .1039
2.0	5.86695	$\bar{1}.9008$	.004953	−5.0056	.004893	− .0758
3.0	5.58445	0.0740	.004247	−5.4595	.004196	− .0075
1.000 Formic Acid, m Sodium Chloride						
	.....	....	0.0	(−3.6300)	0.0	0.0
0.02	7.3508	$\bar{1}.8480$	.01836	−3.6602	.01604	− .0858
.02	7.3569	$\bar{1}.8484$	.01808	−3.6726	.01581	− .0793
.05	6.9772	$\bar{1}.8133$	.01880	−3.7059	.01413	− .0962
.1	6.6877	$\bar{1}.7814$	.01970	−3.7484	.01722	− .1168
.15	6.5263	$\bar{1}.7624$	.01990	−3.8059	.01739	− .1211
.2	6.4045	$\bar{1}.7504$	.02031	−3.8451	.01775	− .1302
2.1253 Formic Acid, m Sodium Chloride						
	.....	....	0.0	(−3.5100)	0.0	0.0
.01	7.4350	$\bar{1}.8448$	.03047	−3.5546	.02288	− .0754
.01	7.4284	$\bar{1}.8440$	.03099	−3.5411	.02328	− .0829
.05	6.7464	$\bar{1}.8024$	.03280	−3.5769	.02463	− .1076
.1	6.4573	$\bar{1}.7750$	.03399	−3.6238	.02553	− .1232
.1	6.4585	$\bar{1}.7750$	.03389	−3.6261	.02546	− .1221
.2	6.1677	$\bar{1}.7480$	.03523	−3.7114	.02646	− .1389

and diverges too slightly (to the right of Curve III) to be clearly distinguished on the scale used.

The fact that the value of log k° is thus apparently independent of the salt used in the solutions of finite ionic strength is obviously an indication in favor of the assumption leading to Equation 17, but much stress should not be laid upon this point since high accuracy is not claimed for the potassium chloride series, and exact agreement must depend on the values for γ°_{HCl} in sodium and potassium chloride solutions given by Harned and Åkerlöf.

Curve II in Fig. 2 shows the extrapolation for log K for formic acid. The extrapolation represented by Equation 16 is shown by the solid line and leads to the values of 0.0585 and -3.753 for S and log K, respectively. K therefore equals 1.77×10^{-4} at 25°.

The dashed line is based upon values of m'_H equal to 0.004482, 0.01732 and 0.03015 in 0.1, 1 and 2.13 M salt-free formic acid solutions, respectively, and extrapolates to approximately the same value of log K. From the value of S for formic acid and Equation 17, the true values of the hydrogen-ion concentrations and activity coefficients have been calculated from the apparent values, and included in Table III, Columns 6 and 7.

The values for γ_A for the 0.1 M formic acid–sodium chloride series may be expressed by the same type of equation, which holds for a strong electrolyte in similar solutions. Thus, the equation

$$\log \gamma_A = -\frac{0.5\sqrt{\mu}}{1 + 1.175\sqrt{\mu}} + 0.095\,\mu \qquad (19)$$

is valid up to an ionic strength of 3 to within a maximum deviation of 1.75% and an average deviation of 0.85%. Since the dielectric constant of 0.1 M formic acid is not appreciably different from that of water, we have retained the universal constant of 0.5 derived from the Debye and Hückel theory. This calculation shows that by employing the definition of the ionic activity coefficient of a weak electrolyte which Harned has applied to water, and Harned and Robinson to weak acids and bases, we arrive at the conclusion that these quantities may be numerically and theoretically treated by the same methods that were used in the cases of strong electrolytes.

The Dissociation Constants of Some Weak Bases.—By employing the data of Harned and Robinson on the methylamines and ammonia in aqueous sodium chloride solutions, we can determine only one value of k° for each base. In order to calculate the true dissociation constants, K, from k° we have shown that it is necessary to know the values of the medium effects, S, which require additional data for at least two concentrations of base. Even though exact values of S are unknown, our method of extrapolation can be shown to be applicable to solutions of these bases. In Table IV are shown the values of m'_{OH} determined by Harned and Robinson, and the values of μ' and $(\log k' - \sqrt{\mu'})$ calculated therefrom. These latter are plotted in Fig. 3. Since, on account of the experimental difficulties, the points at high dilution are scattered, it was impossible

TABLE IV

THE EXTRAPOLATION FUNCTIONS FOR WEAK BASES IN SODIUM CHLORIDE SOLUTIONS

0.5030 *M* NH_3, NaCl (*m*)			0.1987 $(CH_3)_2NH$, NaCl (*m*)		
m	m'_{OH}	$\log k' - \sqrt{\mu'}$	*m*	m'_{OH}	$\log k' - \sqrt{\mu'}$
0.0	0.0	(−4.700)	0.0	0.0	(−3.265)
.1	.004382	−4.738	.02	.01178	−3.308
.2	.004683	−4.809	.05	.01273	−3.310
.5	.005159	−4.983	.1	.01403	−3.310
1	.005621	−5.200	.2	.01620	−3.307
1.5	.005776	−5.400	.5	.01879	−3.428
0.1989 CH_3NH_2, NaCl (*m*)			1	.02204	−3.572
0.0	0.0	(−3.340)	1.5	.02410	−3.713
.02	.01098	−3.369	0.1891 $(CH_3)_3N$, NaCl (*m*)		
.05	.01191	−3.369	0.0	0.0	(−4.245)
.1	.01293	−3.383	.1	.004502	−4.283
.2	.01431	−3.418	.2	.005080	−4.306
.5	.01665	−3.537	.5	.006268	−4.379
1	.01857	−3.728	1	.007296	−4.537
1.5	.01984	−3.890	1.5	.008136	−4.665

to determine values of $\log k^\circ$ by depending only on the points below 0.3 μ'. Consequently, the data were plotted to about $1.5\mu'$ and the extrapo-

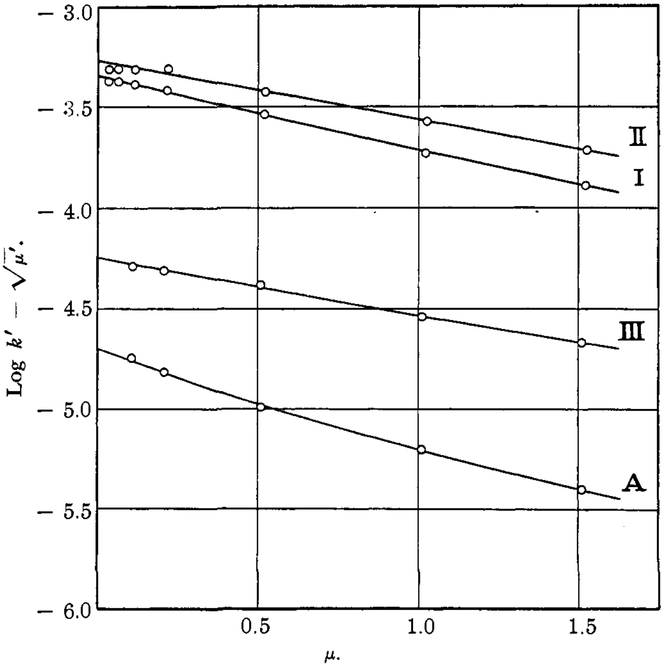

Fig. 3.—Weak bases in sodium chloride solutions. A, 0.503 *M* NH_3; I, 0.199 *M* $NH_2(CH_3)$; II, 0.199 *M* $NH(CH_3)_2$; III, 0.189 *M* $N(CH_3)_3$.

lation was accomplished by the use of long curves in such a way that a straight line was approached at dilute ionic strengths. The values of log k° so obtained are included in Table IV in parentheses. The corresponding values of k° are shown in Table V and compared with the accepted values of K calculated from conductivity measurements. Disregarding for the moment the trimethylamine solutions, our values of k° are all slightly higher than those of K, and our experience with the medium effect would lead us to expect this according to Equation 16. In the absence of sufficient data to evaluate S exactly, we have assumed that the value of 0.047 for S, previously found for acetic acid, is applicable to each basic solution and have calculated the corresponding values of K. These are included in Table V and agree satisfactorily with those derived from conductivity data except in the case of trimethylamine. In this case we believe the discrepancy is considerably greater than the experimental error of the measurements, or in the estimation of the medium effect. It should be mentioned that the medium effect must in all probability be intimately connected with the difference between the dielectric constants of water and the weak electrolyte, and since acetic acid and the bases under consideration have dielectric constants of approximately the same magnitude, our assumption of equality of medium effect is logical. Indeed, for the particular concentrations with which we are dealing, an error of 50% in the assumed value of S would only cause an error of 4.3% in K in the cases of the amines, and of 10% for ammonia.

TABLE V

DISSOCIATION CONSTANTS OF WEAK BASES × 10^{-5}

Source	NH_3	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$
"Int. Crit. Tables," Vol. VI	1.81	40.0	50.0	6.50
This paper (K)	1.79	43.8	52.0	5.45
This paper (k°)	2.00	45.7	54.3	5.69

Conclusions and Summary

1. By the use of the extrapolation function, (log $k' - \sqrt{\mu'}$), we have evaluated the dissociation constants of acetic and formic acids from measurements of cells without liquid junction. This method is thermodynamically sound, and employs no extra-thermodynamical postulates. The accuracy of the numerical values obtained depends entirely upon the validity of the empirical extrapolation function used, and the accuracy of the experimental data.

2. By means of Equation 17, the hydrogen-ion concentrations and ionic activity coefficients may be computed in aqueous solutions containing both the weak acid and salts at various concentrations. The logarithm of the activity coefficients of these electrolytes, referred to unity at infinite dilution in water, varies linearly with the weak acid concentration according to the law expressed by Equations 16 and 17. This law is valid at zero

ionic strength and, further, we believe that it is valid, or very nearly so at all salt concentrations. This latter statement may be verified by computing the activity coefficients relative to unity in a given solvent at various concentrations of the undissociated acid molecule. The results thus obtained agree reasonably with what is to be expected according to the Debye and Hückel theory. Since Harned and Robinson considered this matter, we have not considered it in detail in the present investigation.

3. Our value of 1.75×10^{-5} for the dissociation constant of acetic acid agrees closely with 1.785×10^{-5}, recently computed by Davies[8] by applying viscosity corrections to the conductivity data of Kendall.[9] On the other hand, our value of 1.77×10^{-4} for formic acid is considerably lower than 1.87×10^{-4} obtained by Davies with an extrapolation of Auerbach and Zeglin's[10] conductivity data at 18°.

4. Values for the dissociation constants of ammonia, and the mono-, di- and trimethylamines were computed by the same method from Harned and Robinson's data, and compared with those recently compiled.

5. The present investigation, following that of Harned and Robinson, demonstrates how it is possible, from measurements of cells without liquid junction, to evaluate the thermodynamic behaviors of weak acids and bases in salt solutions, and to determine their dissociation constants by a method which is thermodynamically exact.

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

THE ACID AND BASE CONSTANTS OF GLYCINE FROM CELLS WITHOUT LIQUID JUNCTION[1]

BY HERBERT S. HARNED AND BENTON B. OWEN

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In this study of aqueous solutions of glycine, we shall assume with Bjerrum[2] that the neutral ampholyte molecule in solution exists as "zwitterion," to be designated hereafter "amphion," but our numerical results do not depend upon the validity of this assumption. We further assume complete dissociation of sodium glycinate and glycine hydrochloride in the solutions with which we are concerned, thus

$$ClNH_3CH_2COOH \longrightarrow Cl^- + {}^+NH_3CH_2COOH, \text{ and}$$
$$NH_2CH_2COONa \longrightarrow Na^+ + NH_2CH_2COO^-$$

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[8] Davies, *Phil. Mag.*, [7] **4**, 244 (1927).

[9] Kendall, *J. Chem. Soc.*, **101**, 1285 (1912).

[10] Auerbach and Zeglin, *Z. physik. Chem.*, **103**, 191 (1923).

[1] This paper represents part of the dissertation presented by Benton B. Owen to the Graduate School of Yale University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Bjerrum, *Z. physik Chem.*, **104**, 147 (1923).