DETERMINATION OF THE IONIZATION AND THERMODYNAMIC PROPERTIES OF WEAK ELECTROLYTES BY MEANS OF CELLS WITHOUT LIQUID JUNCTIONS

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The first application of electromotive force measurements of cells without liquid junctions to the study of weak electrolytes was the calculation of the ionization product, $m_H m_{OH}$, and the corresponding activity coefficient function, $\gamma_H \gamma_{OH}/a_{H_2O}$, for water in salt solutions at 25°C. (15, 38, 46). The corresponding puantities for a weak acid were investigated somewhat later by suitable cells containing an unbuffered solution of acetic acid (43) and various salts. The calculations involved the use of ionization constants determined by other methods, notably the conductance method.

In a later contribution a very thorough investigation of the thermodynamics of such cells containing unbuffered acids was made (41). It was shown that ionization constants and the effect of undissociated acid molecules could be evaluated from the electromotive force data alone. From this stage the use of cells without liquid junctions has expanded rapidly and has been applied to a wide variety of systems which include acids, bases, and ampholytes. Much of this work has been carried out over considerable temperature ranges, and some has involved mixed solvents to introduce the effect of variations in the dielectric constant. ΔH^0, ΔS^0, and ΔC_p^0 for the ionization process at unit activities in pure water, mixed solvent, and salt solutions can be estimated from the proper temperature coefficients. In order to present the results in the simplest possible manner, we will disregard chronological order and develop the subject systematically after a general examination of the fundamental aspects of the method.

1. GENERAL CONSIDERATIONS AND LIMITATIONS OF THE METHOD

The fundamental basis of the method consists in computing the concentration of hydrogen ions (protons + solvated ions) in an unknown solution, containing a weak acid, from that of a known concentration of hydrogen ions in a solution of a halogen acid by suitable cell combinations. Its exactness in real solutions, that is to say, solutions other than at zero

ionic strength, will depend on the certainty with which the hydrogen-ion concentration of the halogen acid solution is known. To be explicit, consider the usual method of treatment of the cell,

$$H_2 \mid HX(m) \mid AgX\text{–}Ag$$
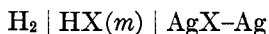
containing a strong halogen acid solution of molality m. The electromotive force, E, of this cell is given by the equation,

$$\begin{aligned} E &= E_0 - RT/\mathbf{F} \ln a_H a_{Cl} \\ &= E_0 - RT/\mathbf{F} \ln \gamma_H \gamma_{Cl} m_H m_{Cl} \end{aligned} \quad (1)$$

where $a_H a_{Cl}$, $\gamma_H \gamma_{Cl}$, and $m_H m_{Cl}$ are, respectively, the activity, activity coefficient, and stoichiometric molality products of the acid in the solution. The meaning to be attached to the quantities γ_H, γ_{Cl}, m_H, and m_{Cl} is largely to be derived from extrathermodynamical knowledge. The subscripts are a convenient symbolism for expressing various combinations of cells and gain significance with the development of the theory and its experimental proof.

All the evidence derivable from modern theory and experiment indicates that hydrochloric acid is a very strong electrolyte. We shall assume that it is completely ionized, and that consequently m_H is the sum of the molal concentrations of protons and solvated protons, and m_{Cl} that of the chloride and solvated chloride ions at all ionic strengths. Any actual deviations from this hypothesis of completely ionized hydrochloric acid which may be brought to light by future investigations will necessitate corrections throughout certain of the subsequent computations. However, such corrections will become smaller as the ionic strengths of the solutions decrease and will vanish for extrapolated results at infinite dilution of electrolytes. Since m_H and m_{Cl} are the stoichiometric molalities of the sum of all species of hydrogen and chloride ions, $\gamma_H \gamma_{Cl}$ is the corresponding activity coefficient product of acid. Under these conditions, this quantity conforms to that capable of being computed by the Debye and Hückel theory (8).

These considerations may be applied to one of the cells which will form the subject of the next section, namely,

$$H_2 \mid MOH(m_1), \ MX(m_2) \mid AgX\text{–}Ag$$

We shall assume that the strong hydroxide, MOH, is completely ionized, so that m_{OH} is the sum of the molalities of the hydroxyl and any hydrated hydroxyl ions present. The electromotive force of this cell is given by equation 1, but in this case the ionization of the weak electrolyte, water, will introduce a fundamental thermodynamic relationship which, when

combined with equation 1, will produce fruitful results. For the ionization constant of water, K_w, we write,

$$K_w = \frac{\gamma_H \, \gamma_{OH}}{a_{H_2O}^x} m_H m_{OH} \qquad (2)$$

where m_H is again the sum of the molalities of the protons and solvated hydrogen ions, $\gamma_H \gamma_{OH}/a_{H_2O}^x$ is an activity coefficient product, and x is unity or greater. By elimination of m_H from equations 1 and 2, we obtain for the electromotive force, E_A, by suitable rearrangement, equations from which K_w, $m_H m_{OH}$, and $\gamma_H \gamma_{OH}/a_{H_2O}^x$ may be computed. The point which should be emphasized so that no misunderstanding may arise is that this method gives K_w exactly and $m_H m_{OH}$ exactly if all strong electrolytes present in the cells are completely ionized. The interpretation of the activity coefficient function depends on the mechanism of the reaction and is not definitely determined by the cell mechanism. If the ionization takes place only according to the reaction,

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$
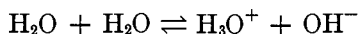
then the activity coefficient function is

$$\frac{\gamma_{H_3O^+} \gamma_{OH^-}}{a_{H_2O}^2}$$

Since cell measurements alone cannot determine the solvation of ions, we shall employ the more vague but simpler symbolism of equation 2, with $x = 1$.

These considerations hold also for all subsequent computations in cases of cells containing weak acids and ampholytes. Ionization constants may be determined exactly, and ionic concentrations may also be determined exactly provided that all strong electrolytes present in the cells are completely ionized. Future knowledge should make it possible to correct discrepancies due to this latter assumption.

2. THE DETERMINATION OF THE IONIZATION CONSTANT OF WATER

The cells employed for the determination of the ionization constant of water are:

I	$H_2 \mid HX(m) \mid AgX–Ag$
II	$H_2 \mid MOH(m_1), MX(m_2) \mid AgX–Ag$
III	$H_2 \mid HCl(m_1), MX(m_2) \mid AgX–Ag$

K_w may be determined from cells I and II (method 1) or from cells II and III (method 2).

Method 1. The electromotive force of cells of type II is given by the equation

$$E_{II} = E_0 - RT/N\mathbf{F} \ln \gamma_H \gamma_X m'_H m'_X \qquad (1a)$$

By combination of this equation and equation 2, and rearrangement of the resulting terms in a convenient form, we obtain

$$\frac{(E_{II} - E_0)N\mathbf{F}}{2.303RT} + \log \frac{m'_X}{m'_{OH}} = \log \frac{\gamma_H \gamma_{OH}}{a^x_{H_2O}} - \log \gamma_H \gamma_X - \log K_w \qquad (3)$$

If the left side of this equation is plotted against the ionic strength, μ, its value at zero μ equals $(-\log K_w)$, since a_{H_2O} and all ionic activity coefficients equal unity, and therefore all terms containing them vanish. Cells of this type were employed by Roberts (72), who used equal concentrations of MX and MOH, thus eliminating the second term on the left, and also by a number of investigators (21, 22, 31, 32, 33, 40, 44), who employed ratios of m_X to m_{OH} greater than unity. The standard potential, E_0, may be determined by either cells I or cells III. In either case the extrapolation was made by employing the Debye and Hückel limiting equation.

Method 2. If we subtract the electromotive forces of cells III, E_{III}, from those of cells II, we obtain

$$\frac{(E_{II} - E_{III})N\mathbf{F}}{2.303RT} = \log \frac{\gamma''_H \gamma''_X m''_H m''_X}{\gamma'_H \gamma'_X m'_H m'_X} = \log \frac{m''_H m''_X}{m'_H m'_X} \qquad (4)$$

where the primes and double primes refer to cells II and III, respectively. The equality to the right introduces the premise that the activity coefficient of the acid is the same in the acid–halide mixtures as in the hydroxide–halide mixtures of the same ionic strength. This assumption is closely approximated, since both the acid and hydroxide are at sufficiently low concentrations (~ 0.01 M or less). If we substitute for m'_H in equation 4 its value derivable from equation 2, we obtain

$$\frac{(E_{II} - E_{III})N\mathbf{F}}{2.303RT} = \log \frac{m''_H m''_X m'_{OH}}{m'_X} + \log \frac{\gamma_H \gamma_{OH}}{a_{H_2O}} - \log K_w \qquad (5)$$

A suitable extrapolation function can be derived from the limiting law of the theory of Debye and Hückel, for, according to this theory,

$$\ln \frac{\gamma_H \gamma_{OH}}{a_{H_2O}} = -\frac{5.908 \times 10^6}{D^{3/2} T^{3/2}} \sqrt{2\mu} + f(\mu) \qquad (6)$$

Substitution in equation 5 gives, upon rearrangement of terms,

$$\frac{(E_{II} - E_{III})N\mathbf{F}}{2.303RT} - \log \frac{m''_H m''_X m'_{OH}}{m'_X} + \frac{5.908 \times 10^6}{D^{3/2} T^{1/2}} \sqrt{2\mu} =$$

$$= - \log K_w + f(\mu) \quad (7)$$

Since E_{II} and E_{III} are the measured electromotive forces, and m''_H, m''_{Cl}, m'_{OH}, and m'_{Cl} are known molalities, the left side of the equation is known, and if it is plotted against μ, its value at zero μ is $(- \log K_w)$. Such a plot is nearly linear in the dilute solutions.
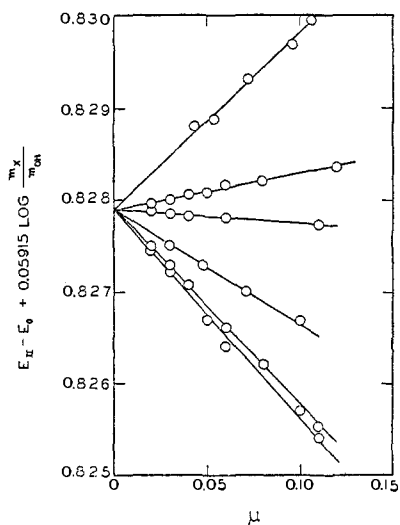

FIG. 1
FIG. 2

FIG. 1. Evaluation of $-0.05915 \log K_w$ by measurements in various salt solutions at 25°C. Reading from top to bottom the salts, MX, are cesium chloride, potassium chloride, sodium chloride, barium chloride, lithium bromide, and lithium chloride.
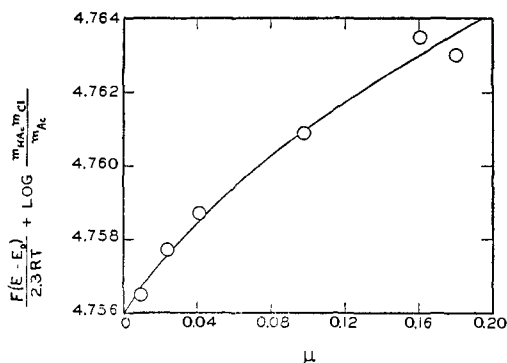
FIG. 2. Evaluation of the ionization constant of acetic acid at 25°C. Diameters of the circles correspond to 0.02 millivolt.

Numerous examples of extrapolations according to equations 3 and 7 have been given in the literature cited above. One graph which is very informative and which clearly illustrates the high accuracy of the method is shown in figure 1. Here

$$\left[E_{II} - E_0 + 2.303RT/N\mathbf{F} \log \frac{m_X}{m_{OH}} \right]$$

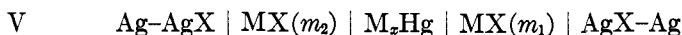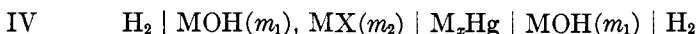at 25°C. is plotted against the total ionic strength, $\mu = m_X + m_{OH}$. Since the coefficient of the third term equals 0.05915, this quantity according to

equation 3 equals $(0.05915 \log \gamma_{OH}/\gamma_X a_{H_2O} - 0.05915 \log K_w)$ at all values of μ and $(- 0.05915 \log K_w)$ when μ equals zero. Results for six salts obtained by as many investigators are plotted. At the lower values of μ these plots are straight lines, and their intercepts at zero μ all lie within 0.05 millivolt. This corresponds to an accuracy of ± 0.1 per cent in the determination of K_w. In all these cases m_{OH} was kept at 0.01, and m_X varied.

In addition, we note that at finite values of μ these results can be used to evaluate the interesting stoichiometrical activity coefficient ratio, γ_{OH}/γ_X, in the salt solutions designated. This result in itself is of considerable interest in connection with the theory of interaction of ions in solutions of finite ionic strength.

3. THE DETERMINATION OF THE ACTIVITY COEFFICIENT FUNCTION, $\gamma_H \gamma_{OH}/a_{H_2O}$, AND THE IONIZATION PRODUCT, $m_H m_{OH}$, IN SALT SOLUTIONS

In addition to cells I, II, and III, the cells

IV $H_2 \mid MOH(m_1), MX(m_2) \mid M_xHg \mid MOH(m_1) \mid H_2$

V $Ag–AgX \mid MX(m_2) \mid M_xHg \mid MX(m_1) \mid AgX–Ag$

have been employed in these investigations of the thermodynamics of ionized water in salt solutions. The first determinations of the quantity, $\gamma_H \gamma_{OH}/a_{H_2O}$ (equation 2) were made by Harned (15), Harned and Swindells (46), Harned and James (38), and Harned and Schupp (44) by means of measurements of cells of types III, IV, and V by a method which is essentially the same as that which will now be described.

(1) Cell III may be used to determine $\gamma_H \gamma_X$ at any concentration in a halide solution of any concentration. Therefore, starting with values of $\gamma_H \gamma_X$ at various concentrations at a given constant molality, it is a simple matter to extrapolate to zero acid concentration and obtain $\gamma_H \gamma_X$ at zero concentration of acid in the pure aqueous halide solution (16).

(2) Similarly, $\gamma_M \gamma_{OH}/a_{H_2O}$ at zero hydroxide-ion concentration, that is to say in pure salt solution, may be obtained from cells of type IV.

(3) From cells of type V, $\gamma_M \gamma_X$ in the pure aqueous salt solution at the same molality may be determined.

(4) Since all these quantities have been evaluated in the pure halide solution, they may be combined without any loss of accuracy. Thus, by multiplying the first two and dividing by the third, we obtain

$$(\gamma_H \gamma_X) \left(\frac{\gamma_M \gamma_{OH}}{a_{H_2O}} \right) \left(\frac{1}{\gamma_M \gamma_X} \right) = \frac{\gamma_H \gamma_{OH}}{a_{H_2O}} \tag{8}$$

which gives us the desired quantity at one salt concentration.

This method is theoretically sound and yields good results but requires measurements of the more cumbersome flowing amalgam cells and incorporates the combined errors of the three types of cells. This method has been superseded by a procedure which involves cells of types II and III.

The equation for cells III may be written,

$$\log \gamma_H \gamma_X = -\frac{F}{2.303RT} (E_{III} - E_0) - \log m_H'' m_X'' \tag{9}$$

Equation 3 may be stated in the form

$$\log \frac{\gamma_H \gamma_{OH}}{a_{H_2O}} = \frac{F}{2.303RT} (E_{II} - E_0) + \log \gamma_H \gamma_X + \log \frac{m_X'}{m_{OH}'} + \log K_w \tag{10}$$

from which $\gamma_H \gamma_{OH}/a_{H_2O}$ may be determined from a knowledge of the standard potential, E_0, and the values of $\gamma_H \gamma_X$ derivable from equation 9. It is convenient to combine these equations and compute $\gamma_H \gamma_{OH}/a_{H_2O}$ by means of the relation,

$$\log \gamma_H \gamma_{OH}/a_{H_2O} = \frac{F}{2.303RT} (E_{II} - E_{III}) - \log \frac{m_H'' m_X'' m_{OH}'}{m_X'} + \log K_w \tag{11}$$

Finally, combination with equation 2 gives

$$-\log m_H m_{OH} = \frac{F}{2.303RT} (E_{II} - E_{III}) - \log \frac{m_H'' m_X'' m_{OH}'}{m_X'} \tag{12}$$

from which the ionization, $m_H m_{OH}$, in the halide solutions may be obtained directly from the molalities of the electrolytes and the electromotive forces.

In the investigations above mentioned, $\gamma_H \gamma_{OH}/a_{H_2O}$ and $m_H m_{OH}$ have been evaluated from 0° to 50°C. in cesium (44), potassium (32), sodium (40), and lithium (21) chloride solutions, potassium (33), sodium (33), and lithium (22) bromide solutions, and barium (31) chloride solutions. In these and other contributions (18) the results have been tabulated and discussed. The methods of obtaining the derived heat data have also received attention. Since the results have been discussed in detail in the above contribution (18), further specialized discussion of them will be omitted.

On the other hand, there is something to be said regarding the accuracy of the determination of the ionization, $m_H m_{OH}$, in the halide solutions. It has been shown (section 1) that if all the electrolytes employed in the cells are completely ionized at all concentrations, then $m_H m_{OH}$ is exactly determined. Evidence from thermodynamic and conductance data shows that hydrochloric acid, hydrobromic acid, and the alkaline halides are very strong electrolytes, so that corrections in the values of $m_H m_{OH}$ from this source will be small. The hydroxides are also strong electrolytes, but

there is evidence that lithium hydroxide and, to a less extent, sodium hydroxide form associated ionic pairs. Potassium and cesium hydroxides are very strong. The fact that the plot of equivalent conductance against square root of the concentration for lithium hydroxide does not lie below the Onsager slope at any concentration indicates that any corrections in these results due to ionic association will not be of large magnitude.

4. IONIZATION CONSTANTS OF WEAK ACIDS AND BASES

The simplest and most direct determination of the ionization constant of a weak acid is based upon measurements of the electromotive forces of cells of the type (24, 25)

VI $H_2 \mid HR(m_1), MR(m_2), MCl(m_3) \mid AgCl–Ag$

Although such cells have been limited to the determination of dissociation constants only, they are peculiarly well adapted to this purpose. Buffer action permits accurate and easy measurements at small hydrogen-ion concentrations and at relatively low ionic strengths. The necessary extrapolation is practically linear except when carried out in media of low dielectric constant and does not require numerous experimental data. The concentrations of the weak acid, HR, and the two salts, MR and MCl, are made approximately equal, and the cation M is usually sodium or potassium. The use of chlorides and the silver–silver chloride electrode has many practical advantages, but other combinations will suggest themselves in special cases. The electromotive force of this cell is given by the same equation as for cells I, II, and III, namely,

$$E = E_0 - \frac{2.3RT}{F} \log \gamma_H \gamma_{Cl} m_H m_{Cl} \qquad (13)$$

As before, E_0 is the electromotive force of the cell

$$H_2 \mid HCl \mid AgCl–Ag$$

at unit activity. The product, $\gamma_H m_H$, can be eliminated by combination with the expression for the ionization of the weak electrolyte,

$$K_A = \frac{\gamma_H \gamma_R}{\gamma_{HR}} \frac{m_H m_R}{m_{HR}}$$

Thus the equation

$$\frac{(E - E^0)F}{2.3RT} + \log \frac{m_{Cl} m_{HR}}{m_R} = -\log K_A - \log \frac{\gamma_{Cl} \gamma_{HR}}{\gamma_R} \qquad (14)$$

is obtained. The terms of the left-hand side are all experimentally determinable, since $m_{Cl} = m_3$, $m_{HR} = m_1 - m_H$, $m_R = m_2 + m_H$, and

m_H may be estimated with sufficient accuracy by a short series of successive approximations explained elsewhere (24, 57, 67). The last term on the right contains the logarithm of the activity coefficient ratio of two univalent ions and the logarithm of the activity coefficient of a neutral molecule, both of which are known to vary linearly with the ionic strength at high dilution. Accordingly, a plot of the left-hand member of equation 14 against the ionic strength, μ, permits the determination of $-\log K_A$ by extrapolation to $\mu = 0$. Figure 2 illustrates the extrapolation by which the dissociation constant of acetic acid is evaluated at 25°C. (24). The extrapolated value of K_A is 1.754×10^{-5}, which is in almost exact agreement with the value 1.758×10^{-5} obtained by conductance measurements (53) and 1.75×10^{-5} derived from electromotive force data on unbuffered solutions (41). Ionization constants of the order of 10^{-3} or 10^{-2} cannot be determined by this method with the same precision because of the increased difficulty of estimating m_H for use in equation 14 (14).

In the case of polybasic acids the extrapolation function is complicated by stepwise dissociation and the presence of polyvalent ions, but this is of little practical importance if the ratios of the constants of the several dissociation processes are greater than 10^3 or 10^4. The second ionization constant of phosphoric acid is especially well suited for determination by this method and will be used to outline the details of the calculations (57). The cel may be represented by

VII $\qquad$ $H_2 \mid MH_2PO_4(m_1), M_2HPO_4(m_2), MCl \mid AgCl-Ag$
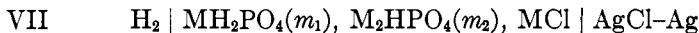
and its electromotive force by equation 1. The second dissociation constant of phosphoric acid is given by

$$K_{2A} = \frac{\gamma_H\, \gamma_{HPO_4}}{\gamma_{H_2PO_4}} \frac{m_H\, m_{HPO_4}}{m_{H_2PO_4}} \tag{15}$$

which leads to

$$\frac{(E - E_0)F}{2.303RT} + \log \frac{m_{Cl}\, m_{H_2PO_4}}{m_{HPO_4}} = -\log K_{2A} - \log \frac{\gamma_{Cl}\gamma_{H_2PO_4}}{\gamma_{HPO_4}} \tag{16}$$

by elimination of $\gamma_H m_H$ with equation 1. The last term on the right contains the activity coefficients of two univalent ions in the numerator and of a bivalent ion in the denominator. Application of the Debye–Hückel equation to this term allows its replacement by $-2S\sqrt{\mu} \pm \beta\mu$ at high dilution. Combining all known quantities in the left member, equation 16 becomes

$$\left[\frac{(E - E_0)F}{2.303RT} + \log \frac{m_{Cl}m_{H_2PO_4}}{m_{HPO_4}} + 2S\sqrt{\mu} \right] = -\log K_{2A} \pm \beta\mu \tag{17}$$

The value of the constant $\pm\beta$ is not determined by present theory, but this is immaterial because it is introduced solely to indicate that a plot of the bracketed member of equation 17 against μ should be linear at high dilution and permit the evaluation of $-\log K_{2A}$ by extrapolation. Figure 3 illustrates the extrapolation at 25°C. (57).

It is interesting to note that, in the phosphate buffer solutions employed, the value of m_H is of the order 10^{-7}, which is so small relative to m_1 and m_2 that it may be disregarded in computing $m_{H_2PO_4}$ and m_{HPO_4}. If, however, m_H is very much less than 10^{-7}, the effects of the hydroxyl-ion concentration and hydrolysis of the acid anion must be taken into account. In general practice it will be found that both m_H and m_{OH} may be neglected

if $\dfrac{m_1}{m_2} \simeq 1$ and K is between 10^{-5} and 10^{-9}.
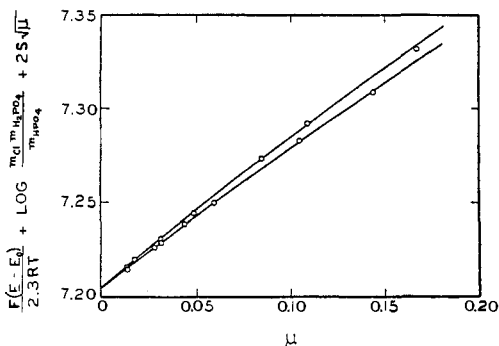
FIG. 3. Evaluation of the second ionization constant of phosphoric acid at 25°C Lower curve: sodium salts, $m_1 = m_2$. Upper curve: monosodium phosphate and dipotassium phosphate, $4m_1 = 3m_2$.

The dissociation constant of HBO_2, or perhaps more properly the first dissociation constant of H_3BO_3, is so small (ca. 6×10^{-10}) that m_{OH} must be considered at high dilution. In this case $m_{HR} = m_1 + m_{OH}$, $m_R = m_2 - m_{OH}$, and $m_{OH} \simeq K_h \dfrac{m_2}{m_1}$ can be estimated with sufficient accuracy from a rough approximation of the hydrolysis constant, K_h, of the acid anion. The tendency of boron to form complex acids in concentrated solution results in a peculiar plot of the extrapolation function of equation 14. Figure 4 illustrates its behavior at 25°C. (67). The ratio m_1/m_2 is 1 in the upper curve, about 1.2 in the short central curve, and about 2.7 in the lower curve. It should be remarked that the upper curve is practically horizontal below $\mu \simeq 0.01$, which makes extrapolation of that series unnecessary beyond this point. Furthermore, equation 14 may be used to determine E_0 once K_A has been evaluated. The combination of

these circumstances and the stability of iodides in alkaline solutions has made it possible to determine E_0 for the silver–silver iodide electrode (69) with much greater ease than by the orthodox use of cells containing dilute hydriodic acid solutions. The use of buffer solutions has been found advantageous in determining other standard electrode potentials (3, 70) as well.

The dissociation constants of weak bases can be determined by a method analogous to that used for acids. Since silver chloride is soluble in ammonia and most amines, some substitute for the silver–silver chloride electrode must be used in many basic systems. The sodium amalgam electrode is known (42) to give results comparable with those of the silver–silver chloride electrode in a system where both can be used, and the use of thallium amalgam has been suggested (73). The silver–silver
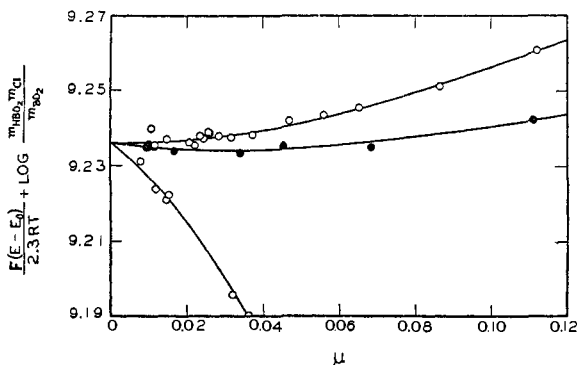
Fig. 4. Evaluation of the ionization constant of boric acid at 25°C. The ratio m_{HBO_2}/m_{BO_2} is 1 in the upper curve, 1.18 in the center curve, and 2.69 in the lower curve.

iodide electrode is the most convenient one for the purpose and will be used to illustrate the method.

The cell can be written

VIII $\qquad$ $H_2 \mid BOH(m_1),\ BI(m_2) \mid AgI\text{–}Ag$

and its electromotive force can be expressed by equation 1 if the substitution of I^- for Cl^- is taken into account. The unknown factor $\gamma_H m_H$ can be eliminated by the introduction of the expressions

$$K_w = \frac{\gamma_H \gamma_{OH}}{a_{H_2O}} m_H m_{OH} \tag{2}$$

and

$$K_B = \frac{\gamma_B \gamma_{OH}}{\gamma_{BOH}} m_B m_{OH} \tag{18}$$

The resulting extrapolation function can be written

$$\left[\frac{(E - E_0)\mathbf{F}}{2.303RT} + \log K_w + \log \frac{m_{\mathrm{B}}m_{\mathrm{I}}}{m_{\mathrm{BOH}}} - \mathbf{S}\sqrt{\mu}\right] = \log K_{\mathrm{B}} \pm \beta\mu \quad (19)$$

after $-\mathbf{S}\sqrt{\mu} \pm \beta\mu$ has been substituted for $\log \gamma_{\mathrm{B}}\gamma_{\mathrm{I}}/\gamma_{\mathrm{BOH}}$. Preliminary measurements on ammonia buffers (68) resulted in a value for K_{B} of the expected order of magnitude. The high vapor pressure of ammonia and its action upon the glass of the cells make it much less amenable to precise investigation than weak acids, so that it has not yet received the attention it deserves. The most reliable values for the dissociation constants of bases are probably the values of K_{B} derived for the basic dissociation of ampholytes discussed in the next section.

5. DETERMINATION OF THE IONIZATION CONSTANTS OF AMPHOLYTES

The determination of the ionization of the most important ampholyte, water, by cells without liquid has been discussed in section 2. The other ampholytes that have been investigated by this method have all been aliphatic amino acids. The neutral molecules of these compounds in solution have been shown (2, 5, 9, 79) to be mainly zwitter ions, or amphions, bearing a positive and negative charge. If such molecules are indicated by $Z^{\pm}$, the acidic and basic dissociation of a simple amino acid may be represented conveniently by

$$ZH^+ \rightleftharpoons Z^{\pm} + H^+ \quad (20)$$

and
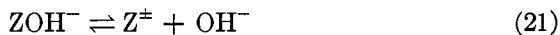
$$ZOH^- \rightleftharpoons Z^{\pm} + OH^- \quad (21)$$

and the corresponding ionization constants by (5, 42)

$$K_{\mathrm{A}} = \frac{\gamma_Z\gamma_{\mathrm{H}}}{\gamma_{\mathrm{ZH}}} \frac{m_Z m_{\mathrm{H}}}{m_{\mathrm{ZH}}} \quad (22)$$

and

$$K_{\mathrm{B}} = \frac{\gamma_Z\gamma_{\mathrm{OH}}}{\gamma_{\mathrm{ZOH}}} \frac{m_Z m_{\mathrm{OH}}}{m_{\mathrm{ZOH}}} \quad (23)$$

The most convenient determination of acidic ionization is performed with cells containing approximately equal concentrations of amino acid and its hydrochloride. Thus for the cell

IX $\qquad$ $\mathrm{H}_2 \mid Z^{\pm}(m_1),\ \mathrm{HCl}(m_2) \mid \mathrm{AgCl\text{-}Ag}$
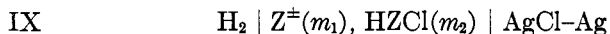
the electromotive force is given by equation 1, and elimination of $\gamma_{\mathrm{H}}m_{\mathrm{H}}$ by equation 22 leads to

$$\frac{(E - E_0)\mathbf{F}}{2.3RT} + \log \frac{m_{\mathrm{Cl}}m_{\mathrm{ZH}}}{m_Z} + \log \frac{\gamma_{\mathrm{Cl}}\gamma_{\mathrm{ZH}}}{\gamma_{Z^-}} = -\log K_{\mathrm{A}} \quad (24)$$

The last term of the left side may be replaced by $-2S\sqrt{\mu} \pm \beta\mu$ and the unknown linear term transposed to give an extrapolation function,

$$\frac{(E - E^0)\mathbf{F}}{2.3RT} + \log \frac{m_{Cl}m_{ZH}}{m_Z} - 2S\sqrt{\mu} = -\log K_A \pm \beta\mu \qquad (25)$$

very similar to that used for phosphoric acid. Since $m_{Cl} = m_2$, $m_Z = m_1 + m_H$, and $m_{ZH} = m_2 - m_H$, the concentration term may be evaluated by successive approximations from a preliminary value of K_A obtained by neglecting m_H altogether. Convergence of successive approximations is rather slow for the amino acids investigated to date because their values
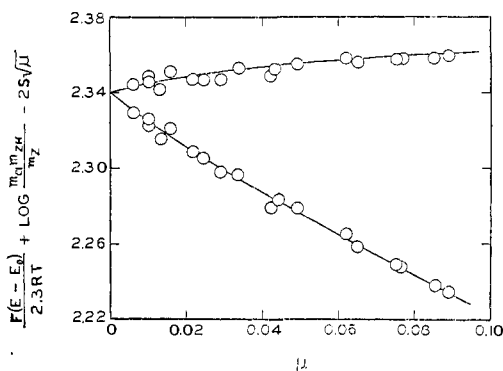
FIG. 5. Determination of the acidic ionization constant of *dl*-alanine at 25°C. In the upper curve $-2S\sqrt{\mu}$ has been replaced by experimental values of $\log \gamma_H\gamma_{Cl}$ in pure sodium chloride solutions.

of K_A are of the order 10^{-3} to 10^{-2}. It is perhaps more satisfactory to rewrite equation 1 as

$$-\log m_H = \frac{(E - E_0)\mathbf{F}}{2.3RT} + \log m_{Cl} + \log \gamma_H \gamma_{Cl} \qquad (26)$$

and estimate m_H with the help of the approximation

$$\log \gamma_H\gamma_{Cl} = -2S\sqrt{\mu}$$

Figure 5 illustrates the use of equation 25 in evaluating K_A for *dl*-alanine (60). At each temperature the lower curve is the plot of the left-hand member of equation 25 against μ. The upper, almost horizontal, curve represents an alternative function obtained by replacing $-2S\sqrt{\mu}$ in equation 25 by known values of $\log \gamma_H\gamma_{Cl}$ in pure aqueous solutions at the ionic strength and temperatures in question. Since both extrapolation functions must give the same value of $-\log K_A$, their difference in slopes is of some practical advantage in accurately locating the common intercept.

The basic ionization constants of ampholytes can be determined by cells of the type

X $H_2 \mid Z^{\pm}(m_1), MZOH(m_2), MCl(m_3) \mid AgCl-Ag$
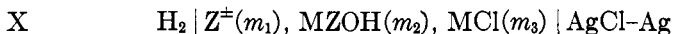
in which the concentrations of the constituents are usually made equal. MZOH represents a convenient alkali (sodium or potassium) salt of the ampholyte and MCl the corresponding chloride. Strictly speaking, the symbol MZOH indicates a hydrated form of the salt, which is here used for convenience in exposition. The question of hydration affects the interpretation of K_B but not its numerical evaluation.

Eliminating $\gamma_H m_H$ and $\gamma_{OH} m_{OH}$ between equations 1 and 23 and the expression for the ionization of water, we obtain

$$\frac{(E - E_0)\mathbf{F}}{2.3RT} + \log \frac{m_{Cl} m_Z}{m_{ZOH}} + \log K_w = \log K_B - \log \frac{\gamma_{Cl} \gamma_Z a_{H_2O}}{\gamma_{ZOH}} \quad (27)$$
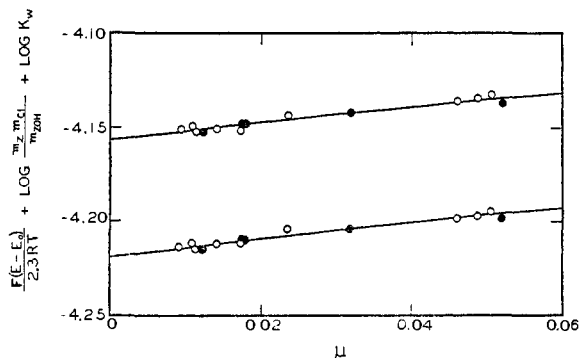
FIG. 6. Evaluation of the basic ionization constant of glycine at 25°C. and 35°C. (upper curve)

The last term on the right involves only neutral molecules and the ratio of two similar ionic activity coefficients. It is therefore linear in μ at high dilution.

Figure 6 illustrates the use of this extrapolation function to evaluate the basic ionization constant of glycine (66).

6. NUMERICAL VALUES OF IONIZATION CONSTANTS AND THE DERIVED THERMODYNAMIC FUNCTIONS, ΔH^0, ΔS^0, AND ΔC_p^0

Tables 1 and 1A summarize the ionization constants obtained by these methods.[1] Only observed values free from temperature smoothing are

[1] While this article was in press, the ionization constants of oxalic acid in water and some methanol-water mixtures were reported by H. C. Parton and R. C. Gibbons (Trans. Faraday Soc. **35**, 542 (1939)) and H. N. Parton and A. J. C. Nicholson (Trans. Faraday Soc. **35**, 546 (1939)).

recorded. In the case of water "best" values from various determinations (31) are given. Two of the acids in table 1 have been independently studied at 25°C. The values $K_A = 1.77 \times 10^{-4}$ for formic acid and $K_A = 1.75 \times 10^{-5}$ for acetic acid were obtained by Harned and Owen (41) in the first calculation of ionization constants from cells without liquid junctions.

There is a discrepancy of 1 or 2 per cent between the independently determined constants of *dl*-alanine that appear in table 1 and those given in table 1A. Whenever the absolute magnitude of K_A or K_B is required the data of table 1 are to be preferred, because the results in table 1A were obtained on very limited quantities of the amino acids and without complete exclusion of air during the cell manipulation. On the other hand, the thermochemical quantities derived from the temperature coefficients of K_A and K_B for alanine are possibly more accurately derived from table 1A because of the longer temperature range.

Precise conductometric determinations, in which proper account was taken of ionic interaction, are now available for a number of acids. *For purposes of comparison all conductometric ionization constants have been converted to a molality basis* by multiplication of the values given in the literature by the specific volume of water at the proper temperature. MacInnes and Shedlovsky (53) found $K_A = 1.758 \times 10^{-5}$ for acetic acid at 25°C. Belcher (4) recently obtained $K_A = 1.347 \times 10^{-5}$ for propionic acid and $K_A = 1.512 \times 10^{-5}$ for *n*-butyric acid at 25°C.

Saxton and Langer (74) and MacInnes, Shedlovsky, and Longsworth (54) reported the almost identical values 1.400×10^{-3} and 1.401×10^{-3} for chloroacetic acid at 25°C. These figures are certainly to be preferred to the lower value in table 1, which required the use of a secondary standard electrode (quinhydrone), but the temperature coefficient and thermal quantities derived from the electromotive force study are probably correct. Martin and Tartar (55) obtained $K_A = 1.391 \times 10^{-4}$ for lactic acid at 25°C. by the usual conductance study over a wide concentration range, and then extended their calculations to other temperatures by measurements on 0.001 normal solutions of lactic acid, potassium lactate, hydrochloric acid, and potassium chloride. Their values at 0° and 50°C. are 1.317×10^{-4} and 1.290×10^{-4}, respectively.

Among the remaining acids in table 1 only phosphoric and sulfuric acids have had their ionization constants estimated by modern conductometric methods. Making use of the data of Abbott and Bray (1) and Noyes and Eastman (62), Sherrill and Noyes (75) obtained $K_{1A} = 8.31 \times 10^{-3}$ for phosphoric acid at 18°C. From the data of Noyes and Stewart (63) they derived the value $K_{2A} = 1.18 \times 10^{-2}$ for sulfuric acid at 25°C. Taking the above comparisons as a whole, the agreement to be expected

TABLE 1

Observed ionization constants

ELECTROLYTE	0°C.	5°C.	10°C.	15°C.	20°C.	25°C.	30°C.	35°C.	40°C.	45°C.	50°C.	55°C.	60°C.	REFERENCE
Formic acid, $K_A \times 10^4$	1.638	1.691	1.728	1.749	1.765	1.772	1.768	1.747	1.716	1.685	1.650	1.607	1.551	(28)
Acetic acid, $K_A \times 10^5$	1.657	1.700	1.729	1.745	1.753	1.754	1.750	1.728	1.703	1.670	1.633	1.589	1.542	(25)
Propionic acid, $K_A \times 10^5$	1.274	1.305	1.326	1.336	1.338	1.336	1.326	1.310	1.280	1.257	1.229	1.195	1.160	(27)
n-Butyric acid, $K_A \times 10^5$	1.563	1.574	1.576	1.569	1.542	1.515	1.484	1.439	1.395	1.347	1.302	1.252	1.199	(45)
Chloroacetic acid, $K_A \times 10^3$	1.528		1.488	1.440†		1.379	1.308‡		1.230					(78)
Lactic acid, $K_A \times 10^4$	1.287		1.361*			1.374		1.336§			1.270			(61)
Glycolic acid, $K_A \times 10^4$	1.334		1.427*			1.475		1.471§			1.415			(59)
Sulfuric acid, $K_{2A} \times 10^2$	1.48	1.43	1.39	1.34	1.27	1.20	1.13	1.05	0.97	0.89	0.79	0.70	0.60	(14)
Phosphoric acid, $K_{1A} \times 10^3$	8.968		8.394*			7.516		6.531§			5.495			(58)
$K_{2A} \times 10^8$					6.056	6.226	6.349	6.430	6.471	6.475	6.439			(57)
Boric acid, $K_{1A} \times 10^{10}$		3.63	4.17	4.72	5.26	5.79	6.34	6.86	7.38		8.32			(67, 69)
Water, $K_w \times 10^{14}$	0.1133	0.1846	0.2920	0.4503	0.6809	1.008	1.468	2.089	2.917	4.018	5.474	7.297	9.614	(31)
Glycine, $K_A \times 10^3$			3.94		4.31	4.47	4.59		4.81					(66)
$K_B \times 10^5$			4.68	5.12	5.57	6.04	6.52	6.98	7.43	7.87				(66)
dl-Alanine, $K_A \times 10^3$					4.47	4.57	4.66	4.71	4.74	4.76				(60)
$K_B \times 10^5$					6.90	7.47	8.08	8.61	9.10	9.60				(60)
Acetic acid in:														
10 per cent methanol, $K_A \times 10^5$	1.138		1.200		1.242	1.247	1.237		1.214					(30)
20 per cent methanol, $K_A \times 10^6$	7.38		7.94		8.24	8.34	8.30		8.19					(30)
20 per cent dioxane, $K_A \times 10^6$	4.75	4.87	4.98	5.05	5.09	5.11	5.08	5.03	4.95	4.86	4.73			(19)
45 per cent dioxane, $K_A \times 10^7$	4.78	4.89	4.96	4.96	4.96	4.93	4.86	4.75	4.61	4.44	4.28			(19)
70 per cent dioxane, $K_A \times 10^9$	4.75	4.83	4.89	4.83	4.83	4.78	4.69	4.56	4.42	4.22	4.05			(19)

* At 12.5°C.   † At 18°C.   ‡ At 32°C.   § At 37.5°C.

between the modern conductance and electromotive force determinations of ionization constants is of the order of 1 per cent.

Space will not permit comparison with all of the estimates of ionization constants obtained from cells involving liquid junctions, but we will present some recent values to show the order of the agreement that can be expected from modern technique and calculations in accord with the interionic attraction theory. The values obtained with liquid junctions

TABLE 1A

Observed ionization constants (76)

ELECTROLYTE	CONSTANTS				
	1°C.	12.5°C.	25°C.	37.5°C.	50°C.
dl-Alanine, $K_A \times 10^3$............................	3.75	4.14	4.49	4.68	4.66
$K_B \times 10^5$............................	4.83	6.10	7.40	8.73	9.86
dl-α-Amino-*n*-butyric acid, $K_A \times 10^3$.............	4.63	4.90	5.18	5.15	5.05
$K_B \times 10^5$.............	4.25	5.50	6.81	8.22	9.38
dl-α-Amino-*n*-valeric acid, $K_A \times 10^3$.............	4.21	4.57	4.81	4.91	4.86
$K_B \times 10^5$.............	4.04	5.18	6.47	7.64	8.63
dl-Norleucine, $K_A \times 10^3$.........................	4.04	4.41	4.62	4.74	4.70
$K_B \times 10^4$.........................	4.41	5.62	6.87	8.05	9.16
α-Aminoisobutyric acid, $K_A \times 10^3$...............	3.81	4.17	4.40	4.46	4.41
$K_B \times 10^4$...............	1.14	1.38	1.61	1.84	1.99
dl-Valine, $K_A \times 10^3$............................	4.79	5.05	5.18	5.11	4.90
$K_B \times 10^5$............................	3.24	4.21	5.27	6.28	7.28
dl-Leucine, $K_A \times 10^3$............................	4.14	4.49	4.70	4.71	4.65
$K_B \times 10^5$............................	3.57	4.52	5.60	6.71	7.59
dl-Isoleucine, $K_A \times 10^3$.........................	4.32	4.59	4.81	4.82	4.66
$K_B \times 10^5$.........................	3.61	4.57	5.77	6.79	7.85

recorded in table 2 were determined by Larsson and Adell (52) at 18°C. The corresponding values from cells without liquid junctions were interpolated to this temperature by means of the constants K_θ and θ given in table 3.

The results in table 1 may be expressed with an average accuracy of the order of 0.002 in log K by the equation of Harned and Embree (29),

$$\log K = \log K_\theta - p(t - \theta)^2 \qquad (28)$$

The concordance of this equation with the data in table 1A is within 0.003 in log K, on the average, with occasional differences as high as 0.007.

K_θ is the value of K at its maximum, θ is the temperature at which K is a maximum, p has the value of 5×10^{-5} deg.$^{-2}$ except for boric acid, in which case 8×10^{-5} was used. The temperature is expressed at $t°$C. Values of the parameters of this equation are recorded in table 3 for all of the electrolytes in tables 1 and 1A except sulfuric acid and water. These last two electrolytes cannot be satisfactorily expressed by an equation of the form of equation 28. In addition to the systems in which the solvent is pure water, all of the results obtained in aqueous mixed solvents by cells without liquid junctions are included at the bottom of table 3. Equation 28 also reproduces these results within their apparent experimental uncertainties. The practical effectiveness of this equation will be further demonstrated in the next section by table 5 in conjunction with equation 54.

TABLE 2

Comparison of ionization constants at 18°C. derived from cells with and without liquid junctions

ACID	WITH LIQUID JUNCTIONS	WITHOUT LIQUID JUNCTIONS
Formic	1.79×10^{-4}	1.76×10^{-4}
Acetic	1.73×10^{-5}	1.75×10^{-5}
Propionic	1.32×10^{-5}	1.34×10^{-5}
n-Butyric	1.53×10^{-5}	1.56×10^{-5}
Chloroacetic	1.49×10^{-3}	1.44×10^{-3}
Lactic	1.38×10^{-4}	1.37×10^{-4}
Glycolic	1.462×10^{-4}	1.355×10^{-4}

The heat content and heat capacity changes of the ionization reaction at unit activities are given by the equations

$$\Delta H^0 = -4.575 \times 10^{-4} T^2 (t - \theta) \tag{29}$$

$$\Delta C_p^0 = -4.575 \times 10^{-4} T(T + 2(t - \theta)) \tag{30}$$

derived by differentiation of equation 28. The free energy and subsequently the entropy changes may be obtained from the customary fundamental thermodynamic relations

$$\Delta F^0 = -2.3026 RT \log K \tag{31}$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta F^0}{T} \tag{32}$$

The equation employed in the estimation of the thermochemical quantities for sulfuric acid is the one given by Hamer (14)
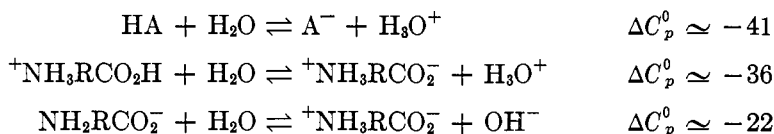
$$\log K_{2A} = -1387.6/T + 1.15612 \log T - 1.355 \times 10^{-5} T$$
$$- 3.8182 \times 10^{-5} T^2 + 3.27632 \tag{33}$$

For the ionization of water we employed the equation

$$\log K_w = -4787.3/T - 7.1321 \log T - 0.010365T + 22.801 \quad (34)$$

given by Harned and Hamer (32). This equation satisfactorily expresses the selected values given in table 1 from 10° to 35°C., but we believe it should not be employed outside this range. This limitation in the use of equation 34 undoubtedly introduces considerable uncertainty in the values of ΔH^0, ΔC_p^0, and ΔS^0 derived from it. This error, due to empirical curve fitting, is inherent in all determinations of thermochemical data from electromotive force measurements, but, other things being equal, it is minimized by studying as large a temperature range as possible. A fair idea of the magnitude of the curve-fitting error can be had by comparing the values in table 3 with those obtained from equations of the form of equation 34 as reported in the original experimental investigations. These values at 25°C. are $\Delta H^0 = -112$, $\Delta C_p^0 = -33.9$ for acetic acid, $\Delta H^0 = -168$, $\Delta C_p^0 = -37.7$ for propionic acid, $\Delta H^0 = -1170$, $\Delta C_p^0 = -34.9$ for chloroacetic acid, and $\Delta H_A^0 = 1159$, $\Delta C_{p_A}^0 = -30.6$, $\Delta H_B^0 = 2765$, $\Delta C_{p_B}^0 = -22.2$ for glycine. With the exceptions of water and sulfuric acid already noted, all of the electrolytes in the tables have been expressed in terms of equation 28. An elaboration of this discussion of the uncertainties of derived quantities, with particular reference to equation 28, can be found in the papers by Walde (77) and Pitzer (71). The latter paper will be given consideration later, because it contains original experimental results and the proposal of a simple two-constant equation to replace equation 28.

One significant generalization, which shows the importance of determining ionization constants as a function of temperature, may be immediately obtained by inspection of table 3. It is clear that no simple inference is to be drawn from the values of ΔF^0, ΔH^0, and ΔS^0, but ΔC_p^0 exhibits some interesting regularities. With the exception of HSO_4^-, H_3PO_4, and $H_2PO_4^-$, the results may be arranged in three groups, corresponding to the type reactions,

$$HA + H_2O \rightleftharpoons A^- + H_3O^+ \qquad \Delta C_p^0 \simeq -41$$

$$^+NH_3RCO_2H + H_2O \rightleftharpoons {}^+NH_3RCO_2^- + H_3O^+ \qquad \Delta C_p^0 \simeq -36$$

$$NH_2RCO_2^- + H_2O \rightleftharpoons {}^+NH_3RCO_2^- + OH^- \qquad \Delta C_p^0 \simeq -22$$

This relationship may be stated in a more significant way by comparing all of the results with a common reference reaction. For this comparison we have chosen the ionization of water,
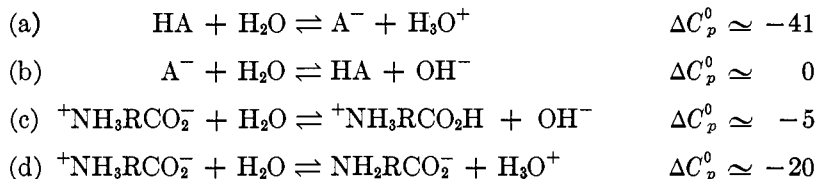
$$H_2O + H_2O \rightleftharpoons OH^- + H_3O^+ \qquad \Delta C_p^0 = -42.5$$

TABLE 3

Parameters of equation 28 and derived thermochemical quantities

ELECTROLYTE	RANGE	θ	$-\log K_\theta$	$-\log K_{25}$	ΔF^0_{25}	ΔH^0_{25}	$\Delta C^0_{p_{25}}$	ΔS^0_{25}
Formic acid	0–50	24.7	3.752	3.752	5117	−12	−40.7	−17.2
Acetic acid	0–45	22.6	4.756	4.756	6486	−98	−41.3	−22.1
Propionic acid	0–45	20.9	4.873	4.874	6647	−167	−41.8	−22.9
Butyric acid	0–45	8.0	4.803	4.817	6569	−691	−45.3	−24.4
Chloroacetic acid	0–35	−5.4	2.815	2.861	3902	−1236	−49.0	−13.9
Lactic acid	0–50	23.5	3.862	3.862	5267	−61	−41.1	−17.9
Glycolic acid	0–50	30.2	3.830	3.831	5225	211	−39.2	−16.8
Sulfuric acid (K_{2A})				1.914	2610	−2229	−91.9	−16.2
Phosphoric acid (K_{1A})	0–50	−18.0	2.030	2.123	2895	−1748	−52.4	−15.6
(K_{2A})	20–50	43.1	7.189	7.205	9826	736	−35.7	−30.5
Boric acid* (K_{1A})	10–50	77.0	9.021	9.237	12597	3382	−42.4	−30.9
Water				13.996	19090	13480	−42.5	−18.8
Glycine (K_A)	10–45	53.9	2.309	2.351	3206	1175	−32.8	−6.8
(K_B)	10–40	93.0	3.988	4.219	5754	2765	−22.1	−10.0
dl-Alanine (K_A)	0–50	44.8	2.330	2.350	3205	805	−35.3	−8.1
(K_B)	0–50	88.0	3.933	4.132	5635	2561	−23.5	−10.3
dl-α-Amino-n-butyric acid (K_A)	0–50	32.6	2.285	2.288	3120	309	−38.6	−9.4
(K_B)	0–50	95.2	3.923	4.169	5686	2854	−21.5	−9.5
dl-α-Amino-n-valeric acid (K_A)	0–50	38.6	2.307	2.316	3159	553	−37.0	−8.7
(K_B)	0–50	92.8	3.965	4.195	5721	2756	−22.2	−10.0
dl-Norleucine (K_A)	0–50	38.8	2.323	2.332	3182	561	−36.9	−8.8
(K_B)	0–50	89.4	3.958	3.165	4316	2618	−23.1	−5.7
α-Aminoisobutyric acid (K_A)	0–50	38.8	2.349	2.359	3217	561	−36.9	−8.9
(K_B)	0–50	75.0	3.667	3.792	5172	2033	−27.0	−10.5
dl-Valine (K_A)	0–50	27.0	2.287	2.287	3119	81	−40.1	−10.2
(K_B)	0–50	97.0	4.022	4.281	5838	894	−34.7	−12.4

dl-Leucine (K_A)	0–50	35.4	2.324	2.329	3176	423	−37.8	−9.2
(K_B)	0–50	93.0	4.022	4.253	5800	2765	−22.1	−10.2
dl-Isoleucine (K_A)	0–50	32.4	2.317	2.320	3164	301	−38.6	−9.6
(K_B)	0–50	93.8	4.009	4.246	5791	2797	−21.9	−10.0
Acetic acid in:								
10 per cent methanol	0–40	27.0	4.904	4.905	6690	81	−40.1	−22.2
20 per cent methanol	0–40	31.5	5.079	5.081	6930	264	−38.9	−22.4
20 per cent dioxane	0–50	24.6	5.293	5.292	7216	−16	−40.8	−24.3
45 per cent dioxane	0–50	15.26	6.305	6.307	8600	−394	−43.3	−30.2
70 per cent dioxane	0–50	10.42	8.313	8.321	11347	−594	−44.6	−40.1

* The results for boric acid have been fitted to equation 28 by making $p = 8 \times 10^{-5}$ instead of the value 5×10^{-5}, which was used for all of the other electrolytes in this table.

although other reactions (e.g., acetic acid) would be suitable. Subtracting the above three reactions in turn from the water reaction, and including the first of them, we obtain

(a) $\quad\quad HA + H_2O \rightleftharpoons A^- + H_3O^+ \quad\quad\quad \Delta C_p^0 \simeq -41$

(b) $\quad\quad A^- + H_2O \rightleftharpoons HA + OH^- \quad\quad\quad \Delta C_p^0 \simeq \quad 0$

(c) $\quad ^+NH_3RCO_2^- + H_2O \rightleftharpoons {}^+NH_3RCO_2H + OH^- \quad \Delta C_p^0 \simeq \quad -5$

(d) $\quad ^+NH_3RCO_2^- + H_2O \rightleftharpoons NH_2RCO_2^- + H_3O^+ \quad \Delta C_p^0 \simeq \quad -20$

Although the deviations from these average values amount to several calories, this classification is surprisingly clear-cut. Consideration of these reactions leads to several important conclusions.

ΔC_p^0 is more closely associated with the type of the reaction than the other thermodynamic quantities ΔF^0, ΔH^0, or ΔS^0. The isoelectric reaction (b) produces practically no change in heat capacity, whereas reaction (a), which forms ions from neutral molecules, produces the greatest change in heat capacity. Reactions (c) and (d) are of the same *electrical* type but give rise to ΔC_p^0 of quite different magnitudes. ΔC_p^0 for reaction (c) is only -5 calories and is, in this respect, similar to the isoelectric type (b), while ΔC_p^0 for reaction (d) is about midway between the isoelectric type and reaction (a), which forms ions from neutral molecules. Furthermore, by subtracting reaction (c) from reaction (d) we obtain a second isoelectric reaction,

(e) $\quad ^+NH_3RCO_2H + OH^- \rightleftharpoons NH_2RCO_2^- + H_3O^+ \quad \Delta C_p^0 \simeq -15$

with another characteristic value of ΔC_p^0. *These considerations show very clearly that the chemical type, as well as the electrical type, of these reactions, is important in determining the magnitude of ΔC_p^0.* It is also brought out by table 3 that ΔC_p^0 for the ionization of acetic acid in aqueous mixed solvents is very nearly the same as that found in pure water, although the dielectric constant has been varied from 78.5 to 17.7.

A theoretical treatment of ionization equilibria involving considerations of molecular dissociation (non-Coulombic forces) and Coulombic forces between the ions is beyond the scope of the present purely thermodynamic discussion, but several papers dealing with this subject should be briefly noted. Moelwyn-Hughes (56) has derived a "semi-empirical" equation for K from kinetic considerations, and Gurney (10) has proposed a theory to separate the non-Coulombic from the electrostatic force effects and has interpreted different types of ionic equilibria on this basis.

Pitzer (71) points out that ΔC_p^0 for most of the electrolytes in table 3 is of the order of -40 calories. If this value is assumed to apply to the

first ionization of all of the electrolytes at all temperatures, their ionization constants may be expressed by the equation

$$\log K = A + B/T - 20 \log T \tag{35}$$

which has the orthodox form of equations 33 and 34 simplified by the assumption regarding ΔC_p^0. He shows that this equation will express the data of table 1 over a wider temperature range than equation 28 and include the data for water as well. This gain in range, however, is obtained at considerable sacrifice in simplicity and ease of calculation, as the two adjustable parameters A and B must be obtained to a relatively large number of significant figures (cf. equations 33 and 34) if log K is to be reproduced within the experimental error. Within the temperature limits given in the second column of table 3 both equations are as good as the experimental data, but equation 28 is to be preferred because of its "slide-rule" convenience.

Pitzer also estimates from theoretical considerations that the entropy of ionization (first hydrogen only) of an acid should be of the order of -22 calories. The agreement of this figure with the average of the results in table 3 is surprisingly good, even in mixed solvents.

7. MIXED SOLVENTS. MEDIUM EFFECT

In discussing the influence of the solvent medium upon the numerical value of the activity coefficient, or ionization constant, of an ionized solute, reference will frequently be made to various medium effects. In a solution of an electrolyte in the presence of neutral (non-aqueous) molecules, the *total medium effect* is defined as the logarithm of the ratio of the activity coefficient of the electrolyte in the presence of the neutral molecules and in pure water at the same concentration of electrolyte. Both of the activity coefficients in this ratio are referred to unity at infinite dilution *in pure water*. The *primary medium effect* is the limit to which the total effect converges as the electrolyte concentration approaches zero. The *secondary medium effect* is always given by the difference between the total and primary effects.

To make use of these terms without confusion, we must be able to identify the reference state of any activity coefficient. Throughout this section all activity coefficients in any medium are understood to be referred to unity at infinite dilution in pure water unless written with an asterisk (*viz.*, γ^*), in which case they are referred to infinite dilution in the medium in which the solute is dissolved. When this medium is pure water, a superscript zero will be used (*viz.*, γ^0, D^0, etc.). A subscript zero indicates that the concentration of electrolyte is zero, except in the conventional

representation of standard potentials such as E_0. Thus for all concentrations, we may write

$$\log \gamma = \log \gamma_0 + \log \gamma^* \qquad (36)$$

or

$$\log \frac{\gamma}{\gamma^0} = \log \gamma_0 + \log \frac{\gamma^*}{\gamma^0} \qquad (37)$$

since $\gamma_0^0 = 1$. This last equation gives the definitional relationship between the total, primary, and secondary medium effects (64) (appearing in that order from left to right).

Born (6) derived the equation

$$\log \gamma_0 = \frac{121}{r} \left(\frac{1}{D} - \frac{1}{D^0} \right) \qquad (38)$$

for the primary medium effect on a uni-univalent electrolyte at 25°C. The effective radius, r, of the ions is defined by $2/r = 1/r_+ + 1/r_-$. Because of the oversimplified physical conditions subsumed in its derivation, this equation is only a rough approximation (65) at best. In mixed solvents in which a change in dielectric constant, D, is accompanied by a large change in the effective molecular weight of the solvent, the observed values of log γ_0 may be much smaller than required by equation 38 and may even assume negative values in some cases (65).

In very dilute solutions the secondary medium effect is given by

$$- \log \frac{\gamma^*}{\gamma^0} = 352 \left\{ \left(\frac{1}{D} \right)^{3/2} - \left(\frac{1}{D^0} \right)^{3/2} \right\} \sqrt{m} \qquad (39)$$

for a uni-univalent electrolyte at 25°C. This equation is, of course, a consequence of the Debye–Hückel limiting law (8) and is a satisfactory expression for the influence of the solvent upon ion–ion interaction at low ionic strengths.

Very few studies of medium effect come within the scope of the title of this review, but they will suffice for purposes of illustration. The primary and total medium effects of undissociated acetic acid molecules upon hydrochloric acid have been directly measured (64) at 25°C., and it has been shown how these quantities may be taken into account in determining the ionization constants of weak electrolytes (35, 41). The primary medium effect of 10 and 20 per cent methanol (30) and of 20, 45, and 70 per cent dioxane (39) on acetic acid has been measured over a wide temperature range.

For simplicity the latter results will be considered first. The cells employed are represented by the following example:

XI $H_2 \mid HR(m_1), NaR(m_2), NaCl(m_3), X$ per cent ethanol $\mid$ AgCl–Ag
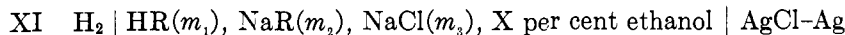
There are two simple thermodynamically equivalent ways of expressing the electromotive force of such a cell, viz.,

$$\frac{F(E - E_0)}{2.3RT} = -\log m_H m_{Cl} - \log \gamma_H \gamma_{Cl} \tag{40}$$

and

$$\frac{F(E - E_0^*)}{2.3RT} = -\log m_H m_{Cl} - \log \gamma_H^* \gamma_{Cl}^* \tag{41}$$

In the first expression $-E_0$ is the standard potential of the silver–silver chloride electrode in pure water. In the second expression $-E_0^*$ is the standard potential in the mixed solvent. Combination of these two equations and comparison with equation 36 show that the primary medium effect of the alcohol upon the hydrogen and chloride ions is directly given by the two standard potentials. Thus

$$\log \gamma_{0HCl} = \frac{1}{2} \log \frac{\gamma_H \gamma_{Cl}}{\gamma_H^* \gamma_{Cl}^*} = \frac{F(E_0 - E_0^*)}{4.6RT} \tag{42}$$

The primary medium effect of alcohol upon the activity coefficient, or ionization constant, of acetic acid can be determined by extrapolation of the data for the above cell in accordance with the procedure outlined in the fourth section of this review. Employing equation 41 we would obtain a quantity K_A^* the value of which is a function of the medium, because γ^* is always unity at infinite dilution. If we write

$$\gamma_A^2 = \frac{\gamma_H \gamma_R}{\gamma_{HR}} \quad \text{and} \quad k_A = \frac{m_H m_R}{m_{HR}}$$

the thermodynamic ionization constant in pure water, K_A, is related by the definitional equation,

$$K_A = \gamma_A^2 k_A = \gamma_{0A}^2 \gamma_A^{*2} k_A = \gamma_{0A}^2 K_A^* \tag{43}$$

to the properties of the acid in the mixed solvent. Accordingly,

$$\log \gamma_{0A} = \frac{1}{2} \log \frac{K_A}{K_A^*} \tag{44}$$

Table 4 contains the values of E_0^* and K_0^* obtained in methanol–water and dioxane–water mixtures and the corresponding values of $\log \gamma_{0HCl}$ and $\log \gamma_{0A}$. The medium effect of acetic acid molecules upon hydrochloric

acid was calculated from the measurements of Owen.[2] It will be noticed that the medium effect of acetic acid upon hydrochloric acid is greater than that of methanol or dioxane and that the effects of the latter upon acetic acid are greater than upon hydrochloric acid. The medium effect of acetic acid molecules upon ionized acetic acid has not yet been determined experimentally, but it will be referred to in the discussion to follow.

If equation 40 were employed for extrapolation instead of equation 41, the situation would be similar, in some respects, to that encountered with cells containing unbuffered solutions of weak acids. The extrapolation equation can be written

$$\left[\frac{\mathbf{F}(E - E_0)}{2.3RT} + \log \frac{m_{\mathrm{R}}}{m_{\mathrm{HR}}} m_{\mathrm{Cl}} \right] = -\log K_{\mathrm{A}} + 2 \log \gamma_{\mathrm{A}} - 2 \log \gamma_{\mathrm{HCl}} \quad (45)$$

TABLE 4

Results in various solvents at 25°C.

SOLVENT	E_0^*	$10^3 \times K_{\mathrm{A}}^*$	LOG $\gamma_{0_{\mathrm{HCl}}}$	LOG $\gamma_{0_{\mathrm{A}}}$
Pure water................	0.22239 (26)†	1754 (25)†	0.0	0.0
10 per cent methanol.....	0.21535 (47)	1247 (30)	0.0595	0.0741
20 per cent methanol.....	0.20881 (47)	833 (30)	0.1148	0.1614
20 per cent dioxane......	0.20303 (17)	511 (19)	0.1636	0.2678
45 per cent dioxane......	0.16352 (23)	49.3 (19)	0.4976	0.7755
70 per cent dioxane......	0.06395 (20)	0.478 (19)	1.3392	1.7823
82 per cent dioxane......	−0.0415 (48)	0.0072‡	2.230	2.69
10 per cent acetic acid...	0.21050 (64)		0.1005	
20 per cent acetic acid...	0.19682 (64)		0.2161	
30 per cent acetic acid...	0.18091 (64)		0.3506	
40 per cent acetic acid...	0.16211 (64)		0.5095	
50 per cent acetic acid...	0.13945 (64)		0.7010	
60 per cent acetic acid...	0.11150 (64)		0.9373	

† Reference to literature.

‡ Preliminary value obtained in this laboratory by Dr. Leslie D. Fallon.

Extrapolation of the left-hand member to zero ionic strength yields $-\log K_{\mathrm{A}} + 2 \log \gamma_{0_{\mathrm{A}}} - 2 \log \gamma_{0_{\mathrm{HCl}}}$, so that, knowing K_{A}, we obtain the *difference* between the primary medium effect of methanol upon the weak acid and hydrochloric acid. From this it is clear that $\log \gamma_{0_{\mathrm{A}}}$ cannot be obtained from the above cell unless either $\log \gamma_{0_{\mathrm{HCl}}}$ or E_0^* is known (cf. equation 42).

We are now in a position to consider unbuffered cells of the type

XII $\mathrm{H_2} \mid \mathrm{HR}(m_1), \; \mathrm{NaCl}(m_2) \mid \mathrm{AgCl\text{-}Ag}$
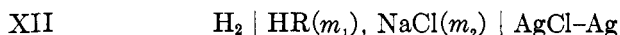
[2] The relation employed is
$$(0.22239 - E_0^*)/0.059155 = \log \gamma_{0_{\mathrm{HCl}}} = 5.87N/2 + \log d/d_0$$
which may be derived from equations 14 and 18 of reference 64.

first used to determine ionization constants (41) and the activity coefficients (43) of weak electrolytes in salt solutions. In such cells the weak acid concentration was maintained constant at some particular value of m_1, while the salt concentration, m_2, was varied. If the electromotive force expression for this cell be rearranged and $2 \log \gamma_{0HCl}$ added to both sides of the equation, we can write

$$\left[\frac{\mathbf{F}(E - E_0)}{2.3RT} + \log m_2 + 2 \log \gamma_{0HCl}\right] = -\log m_H - 2 \log \frac{\gamma_{HCl}}{\gamma_{0HCl}} \quad (46)$$

The right-hand member contains the total medium effect of the weak acid upon the chloride and hydrogen ions. This quantity is ordinarily unknown. We will therefore define an *apparent* hydrogen-ion concentration, m_H', given by

$$\log m_H' = \log m_H + 2 \log \frac{\gamma_{HCl}}{\gamma_{0HCl}} \quad (47)$$

and hence directly calculable from the left-hand member of equation 46. The corresponding apparent activity coefficient of the weak acid is defined in terms of the thermodynamic ionization constant by the equation

$$K_A = \frac{\gamma_H' \gamma_R'}{\gamma_{HR}'} \frac{m_H'^2}{m_1 - m_H'} = \gamma_A'^2 k_A' \quad (48)$$

analogous to the expression

$$K_A = \frac{\gamma_H \gamma_R}{\gamma_{HR}} \frac{m_H^2}{m_1 - m_H} = \gamma_A^2 k_A \quad (49)$$

connecting the real activity coefficient with the real hydrogen-ion concentration. In both of these expressions all activity coefficients are referred to unity at infinite dilution in pure water.

Combining equations 47, 48, and 49, we find that

$$\log \gamma_A' = \log \gamma_A - 2 \log \frac{\gamma_{HCl}}{\gamma_{0HCl}} + \frac{1}{2} \log \frac{m_1 - m_H'}{m_1 - m_H} \quad (50)$$

which shows that $\log \gamma_A'$ is expressed in terms of real activity coefficients and indeed must simulate the properties of a real activity coefficient when the term containing m_H' is small. If the concentration, m_1, of the weak acid is kept constant while the ionic strength is altered by variations in salt concentration, m_2, we can obtain a series of values of m_H' and k_A' in a $m_1 - m_H$ molal solution of unionized weak electrolyte in water. So long as m_H is much smaller than m_1, the composition of the solvent is very nearly constant, and the primary medium effect and, as a first approxi-

mation, the total medium effect may be considered independent of the salt concentration. It is therefore practicable to obtain

$$k'_{0_A} = \frac{\text{Lim.}}{\mu \to 0} k'_A$$

by extrapolation. The logarithm of the corresponding quantity

$$\gamma'_{0_A} = \frac{\text{Lim.}}{\mu \to 0} \gamma'_A$$

is of the nature of a primary medium effect, since it would be

$$\log \gamma_{0_A} - 2 \log \gamma_{0_{HCl}}$$
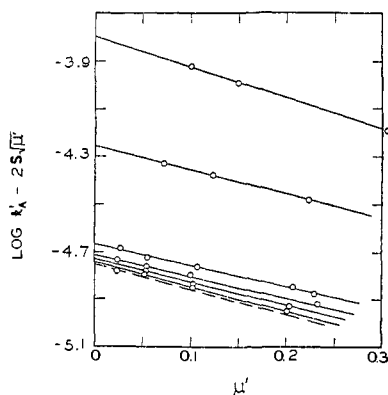
by equation 50 if the concentration term is eliminated by the extrapolation.

FIG. 7. Evaluation of k'_{0_A} for acetic acid at 25°C. for various values of m_1. Reading down, m_1 = 10.2, 5.41, 1.0, 0.52, 0.2, and 0.1. The dashed line represents the hypothetical limiting curve when m_1 = 0.
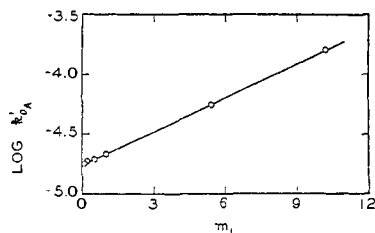
FIG. 8. Evaluation of $\log K_A$ for acetic acid at 25°C.

The extrapolation of $\log k'_A$ is performed by means of the equations

$$\log k'_A - 2S \sqrt{\mu'} = \log k'_{0_A} \pm 2\beta\mu' \tag{51}$$

or

$$\log k'_A - \frac{2S \sqrt{\mu'}}{1 + A \sqrt{\mu'}} = \log k'_{0_A} \pm 2\beta\mu' \tag{52}$$

in which $\mu' = m_2 + m'_H$ is used for $m_2 + m_H$ as a very close approximation. The use of the numerical value of S for pure water neglects the secondary medium effect of the weak acid, but this approximation is unavoidable because the influence of HR molecules upon the dielectric constant of the solvent is generally unknown. The extrapolation is illustrated by figure 7,

in which $\log k'_{0_A}$ is determined for acetic acid (41) for six values of m_1 by equation 51. A recent investigation (35) shows that it is necessary to use equation 52 if higher values of μ' are included.

From the nature of γ'_{0_A} it is clear that it must become unity when $m_1 = 0$, for under this condition the medium is pure water. According to equation 48, extrapolation of k'_{0_A} to $m_1 = 0$ must therefore yield K_A. This second extrapolation is shown in figure 8. The fact that this extrapolation is linear within the experimental error is without theoretical significance, as it is impossible at present to evaluate the effects of the several approximations involved in the calculations. It is known that $\log \gamma_{0_{HCl}}$ is not linear (64) when similarly plotted, but the behavior of $\log \gamma_{0_A}$ is unknown.[3]

The nearly parallel nature of the lines for low concentrations in figure 7 suggests that the broken line drawn from the intercept $\log K_A$ would closely represent the properties of infinitely dilute acetic acid in sodium chloride solutions. On such solutions the medium effect of the weak acid is zero. Therefore, dropping the primes in equation 51 or 52 and referring to equation 49, it follows that the slope of the broken line can be identified with 2β in an equation such as

$$2 \log \gamma_A = \log K - \log k_A = \frac{-2S\sqrt{\mu}}{1 + A\sqrt{\mu}} + 2\beta \qquad (53)$$

which readily permits evaluation of the ionization, or activity coefficient, γ_A, of the weak acid in salt solutions.

Harned and Hickey (35) have determined k_A for acetic acid in sodium chloride solutions by this method from 0° to 40°C. They found that the temperature variation could be expressed by the relation

$$\log k_A = \log k_\vartheta - 5 \times 10^{-5}(t - \vartheta)^2 \qquad (54)$$

similar to equation 28. This leads to the interesting conclusion that $\log \gamma_A$ varies linearly with temperature, for by combining equations 53 and 54 with equation 28 we can obtain

$$\log \gamma_A = 1/2 \log K_\vartheta/k_\vartheta + 2.5 \times 10^{-5}(\vartheta^2 - \theta^2) - 5 \times 10^{-5}(\vartheta - \theta)t \qquad (55)$$

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[3] Owing to an unfortunate oversight in the paper of Harned and Owen (41), the third equality in their equation 17 is invalid, as it neglects the medium effect of acetic acid upon the real γ_A. The third sentence on page 5081 of that paper is also erroneous, as it refers γ_A to "a given solvent" rather than to pure water. These errors were not detected when Owen (64) correctly measured $\log \gamma_{0_{HCl}}$ directly and compared it with the value estimated from equation 17 of reference 47 and the slope of figure 8 of the present review. Although this "comparison" does not serve its original purpose, it might be taken to indicate that the medium effect on γ_A is smaller than that upon γ_{HCl}. It should be noted that the ordinate of figure 4 (reference 64) should have been labelled "$2 \log \gamma_0$", as may be seen from the context.

Values of log k_θ and ϑ are given in table 5. The average deviations between observed values of log k_A and those calculated by equation 54 are indicated by $\Delta_{ave.}$.

The behavior of the activity coefficients of two weak electrolytes in sodium chloride solutions is illustrated in figure 9, where they are compared with the activity coefficient of the strong electrolyte, hydrochloric acid, in the same salt solutions. Although the activity coefficients of

TABLE 5

Parameters of equation 54 for acetic acid in sodium chloride solutions

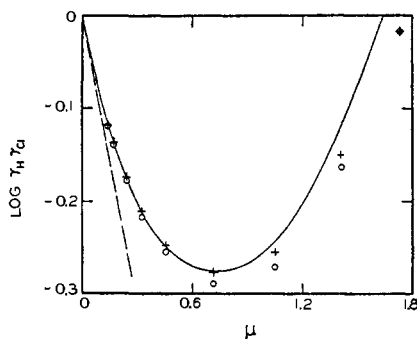| μ	$-$LOG k_ϑ	ϑ	$\Delta_{ave.}$
0.00	4.7544	22.6	0.0009
0.02	4.6388	25.1	0.0007
0.03	4.6189	25.6	0.0007
0.06	4.5798	26.4	0.0007
0.11	4.5432	27.6	0.0009
0.21	4.5061	29.2	0.0011
0.51	4.4752	32.3	0.0009
1.01	4.4957	35.7	0.0012
2.01	4.5875	45.0	0.0029
3.01	4.7132	50.9	0.0038

FIG. 9. Comparison of the activity coefficients of electrolytes in sodium chloride solutions at 25°C. Smooth curve, log $\gamma_{H}\gamma_{Cl}$; $\bigcirc$, log $\gamma_{H}\gamma_{OH}/a_{H_2O}$; $+$, log $\gamma_{H}\gamma_{Ac}/\gamma_{HAc}$.

other weak acids and ampholytes have been studied by means of cells without liquid junctions, they are not included in figure 9, because the corrections for medium effects were incomplete or neglected. A large number of such systems have also been studied by cells with liquid junctions (50, 51, 52), and by catalytic (7, 34) or optical (11, 12, 13) methods.

The simplest interpretation of the close similarity in the behavior of log $\gamma_{H}\gamma_{Cl}$ and log $\gamma_{H}\gamma_{Ac}/\gamma_{HAc}$, or log $\gamma_{H}\gamma_{OH}/a_{H_2O}$, is to infer that the effect of the ionic strength of the salt upon the two terms γ_{HAc} and a_{H_2O} is relatively

insignificant in dilute solutions. The correctness of this inference is born out by theory and by a considerable body of experimental evidence. Using an optical method, von Halban, Kortüm, and Seiler (13) have very accurately separated the activity coefficient function for the weak acid α-dinitrophenol into $\gamma_{\pm}$, for the ionic constituents, and γ_u for the undissociated neutral molecule. They found log γ_u approximately linear in μ. More recently (49) cells without liquid junctions have been used to yield such information. Larson and Tomsicek (49) found that γ_{HAc} in a 0.5 normal acetic solution was changed less than 10 per cent when the ionic strength was increased to unity by addition of potassium acetate.

By combination of the activity coefficients derived for acetic acid (35) with values (40) of $\gamma_w = \gamma_H \gamma_{OH}/a_{H_2O}$, the influence of sodium chloride upon
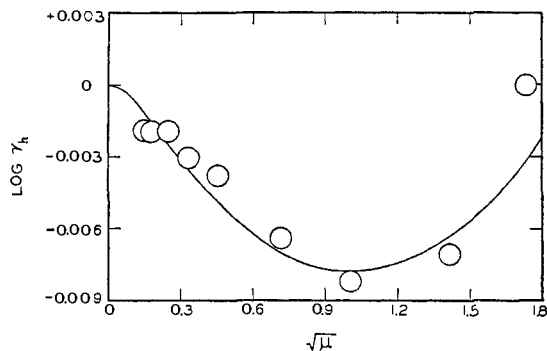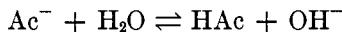

FIG. 10. Variation of log γ_h for hydrolysis of acetate ion in sodium chloride solutions at 25°C.

the hydrolysis of the acetate ion (at infinite dilution) can be readily investigated. The relationship between the hydrolytic reaction,

$$Ac^- + H_2O \rightleftharpoons HAc + OH^-$$

and the ionization reactions of water and acetic acid is

$$K_h = \frac{K_w}{K_A} = \frac{\gamma_{HAc}\gamma_{OH}}{a_{H_2O}\gamma_{Ac}} \frac{m_{HAc}m_{OH}}{m_{Ac}} = \frac{\gamma_w^2}{\gamma_A^2} \frac{k_w}{k_A} = \gamma_h^2 k_h \tag{56}$$

Since the four quantities γ_w, k_w, γ_A, and k_A are separately known in sodium chloride solutions, γ_h and k_h can be evaluated in these solutions. Values of γ_h can be calculated from K_h and k_h tabulated by Harned and Hickey (36, 37). The results at 25°C. are plotted in figure 10 as circles, the radii of which represent an uncertainty of 0.1 per cent in γ_h.

Figure 10 brings out two interesting points. The total variation of γ_h with salt concentration is very small, being less than 2 per cent. This nearly ideal behavior of the hydrolysis reaction maintains also at 30° and

40°C., but tends to disappear at lower temperatures. The second point of interest is the form taken by the plot in dilute solutions. Since γ_h is $\gamma_{HAc}\gamma_{OH}/a_{H_2O}\gamma_{Ac}$ by equation 56, a plot of log γ_h against $\sqrt{\mu}$ must approach the intercept, log $\gamma_h = 0$, with zero slope. It is clear from the figure that this condition is not fulfilled at the lowest experimental concentration, 0.02 M. To illustrate the extreme dilutions which might be required before the plot shows definite signs of becoming horizontal, the curve is drawn for the ratio of two hypothetical univalent ions conforming to the Debye–Hückel equation. The "a" values were taken as 4.0 and 4.5 Å., and a linear term, 0.005 μ, was selected to give approximate agreement with the data at high ionic strengths. The numerical values of these parameters are too arbitrary to be significant individually, but they demonstrate the essential conformity of the data with modern theory, and their difference, 0.5 Å., calls attention to the very small magnitude of the effect which has been measured experimentally.

8. SUMMARY[4]

1. A careful analysis is made of the methods by which the thermodynamic properties of weak electrolytes may be determined in water, in salt solutions, and in mixed solvents by means of cells without liquid junctions. It is shown that thermodynamic ionization constants can be exactly determined by suitable cell measurements, but that the accuracy with which the concentrations of the ions of a weak electrolyte (water) in salt solutions can be determined is limited to the accuracy with which we know the degree of ionization of certain strong electrolytes.

2. Two methods for determining the thermodynamic ionization constant of water are described and illustrated.

3. It is shown how the ionization product, $m_H m_{OH}$, can be evaluated in neutral salt solutions.

4-5. Suitable cells for determining the thermodynamic ionization constants of weak acids, bases, and ampholytes are described in detail. The practical graphical methods employed in the calculations are illustrated by five examples.

6. Numerical values of the ionization constants are tabulated for all of the weak electrolytes, of various types, investigated by these methods. These results are compared with values obtained by conductometric methods and by cells with liquid junctions.

With the exception of the values for water and the hydrosulfate ion, these ionization constants may be expressed by the equation

$$\log K = \log K_\theta - p(t - \theta)^2$$

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[4] The numbering of the paragraphs in the summary is identical with that of the corresponding section headings of this review.

over a 30° to 50°C. temperature interval within the apparent experimental errors. The constant p has the value 5×10^{-5}, except in the case of boric acid, where 8×10^{-5} is used. By means of this equation, ΔF^0, ΔH^0, ΔS^0, and ΔC_p^0 for the ionization reactions at unit activities have been estimated and their values at 25°C. tabulated. It is remarked that ΔC_p^0 is more simply associated with the type of the ionization reaction than the other thermodynamic functions, and certain generalizations of a qualitative nature are pointed out.

7. The formal influence of variations in the solvent medium upon the thermodynamic properties of the solute is presented. By separating this influence into a primary and secondary medium effect, it is shown what quantities may be determined from cell measurements involving mixed solvents. In the light of this information, the interpretation of cell measurements on unbuffered weak acids in salt solutions is treated in some detail. It is shown how the activity coefficients of weak electrolytes may be estimated in neutral salt solutions. The hydrolytic reaction,

$$Ac^- + H_2O \rightleftharpoons HAc + OH^-$$
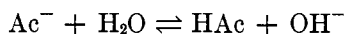
is discussed, and some of the thermodynamic properties of this equilibrium are illustrated.

REFERENCES

(1) ABBOTT, G. A., AND BRAY, W. C.: J. Am. Chem. Soc. **31**, 748 (1909).

(2) ADAMS, E. Q.: J. Am. Chem. Soc. **38**, 1503 (1916).

(3) BATES, R. G., AND VOSBURGH, W. C.: J. Am. Chem. Soc. **59**, 1188 (1937).

(4) BELCHER, D.: J. Am. Chem. Soc. **60**, 2744 (1938).

(5) BJERRUM, N.: Z. physik. Chem. **104**, 147 (1923).

(6) BORN, M.: Z. Physik **1**, 45 (1920).

(7) DAWSON, H. M., AND KEY, A.: Proc. Leeds Phil. Lit. Soc., Sci. Sect. **2**, 296 (1932).

(8) DEBYE, P., AND HÜCKEL, E.: Physik Z. **24**, 185, 305 (1923).

(9) EDSALL, J. T., AND BLANCHARD, M. H.: J. Am. Chem. Soc. **55**, 2337 (1933).

(10) GURNEY, R. W.: J. Chem. Phys. **6**, 499 (1938).

(11) VON HALBAN, H., AND EBERT, L.: Z. physik. Chem. **112**, 359 (1924).

(12) VON HALBAN, H., AND KORTÜM, G.: Z. physik. Chem. **A170**, 351 (1934).

(13) VON HALBAN, H., KORTÜM, G., AND SEILER, M.: Z. physik. Chem. **A173**, 449 (1935).

(14) HAMER, W. J.: J. Am. Chem. Soc. **56**, 860 (1934).

(15) HARNED, H. S.: J. Am. Chem. Soc. **47**, 930 (1925).

(16) HARNED, H. S.: J. Am. Chem. Soc. **48**, 326 (1926).

(17) HARNED, H. S.: J. Am. Chem. Soc. **60**, 336 (1938).

(18) HARNED, H. S.: J. Franklin Inst. **225**, 623 (1938).

(19) HARNED, H. S.: J. Phys. Chem. **43**, 275 (1939).

(20) HARNED, H. S., AND CALMON, C.: J. Am. Chem. Soc. **60**, 2130 (1938).

(21) HARNED, H. S., AND COPSON, H. R.: J. Am. Chem. Soc. **55**, 2206 (1933).

(22) HARNED, H. S., AND DONELSON, J. G.: J. Am. Chem. Soc. **59**, 1280 (1937).

(23) HARNED, H. S., AND DONELSON, J. G.: J. Am. Chem. Soc. **60**, 2128 (1938).
(24) HARNED, H. S., AND EHLERS, R. W.: J. Am. Chem. Soc. **54**, 1350 (1932).
(25) HARNED, H. S., AND EHLERS, R. W.: J. Am. Chem. Soc. **55**, 652 (1933).
(26) HARNED, H. S., AND EHLERS, R. W.: J. Am. Chem. Soc. **55**, 2179 (1933).
(27) HARNED, H. S., AND EHLERS, R. W.: J. Am. Chem. Soc. **55**, 2379 (1933).
(28) HARNED, H. S., AND EMBREE, N. D.: J. Am. Chem. Soc. **56**, 1042 (1934).
(29) HARNED, H. S., AND EMBREE, N. D.: J. Am. Chem. Soc. **56**, 1050 (1934).
(30) HARNED, H. S., AND EMBREE, N. D.: J. Am. Chem. Soc. **57**, 1669 (1935).
(31) HARNED, H. S., AND GEARY, C. G.: J. Am. Chem. Soc. **59**, 2032 (1937).
(32) HARNED, H. S., AND HAMER, W. J.: J. Am. Chem. Soc. **55**, 2194 (1933).
(33) HARNED, H. S., AND HAMER, W. J.: J. Am. Chem. Soc. **55**, 4496 (1933).
(34) HARNED, H. S., AND HAWKINS, J. E.: J. Am. Chem. Soc. **50**, 85 (1928).
(35) HARNED, H. S., AND HICKEY, F. C.: J. Am. Chem. Soc. **59**, 1284 (1937).
(36) HARNED, H. S., AND HICKEY, F. C.: J. Am. Chem. Soc. **59**, 1289 (1937).
(37) HARNED, H. S., AND HICKEY, F. C.: J. Am. Chem. Soc. **59**, 2303 (1937).
(38) HARNED, H. S., AND JAMES, G. M.: J. Phys. Chem. **30**, 1060 (1926).
(39) HARNED, H. S., AND KAZANJIAN, G. L.: J. Am. Chem. Soc. **58**, 1912 (1936).
(40) HARNED, H. S., AND MANNWEILER, G. E.: J. Am. Chem. Soc. **57**, 1873 (1935).
(41) HARNED, H. S., AND OWEN, B. B.: J. Am. Chem. Soc. **52**, 5079 (1930).
(42) HARNED, H. S., AND OWEN, B. B.: J. Am. Chem. Soc. **52**, 5091 (1930).
(43) HARNED, H. S., AND ROBINSON, R. A.: J. Am. Chem. Soc. **50**, 3157 (1928).
(44) HARNED, H. S., AND SCHUPP, O. E., JR.: J. Am. Chem. Soc. **52**, 3892 (1930).
(45) HARNED, H. S., AND SUTHERLAND, R. O.: J. Am. Chem. Soc. **56**, 2039 (1934).
(46) HARNED, H. S., AND SWINDELLS, F. E.: J. Am. Chem. Soc. **48**, 126 (1926).
(47) HARNED, H. S., AND THOMAS, H. C.: J. Am. Chem. Soc. **57**, 1666 (1935).
(48) HARNED, H. S., WALKER, F., AND CALMON, C.: J. Am. Chem. Soc. **61**, 44 (1939).
(49) LARSON, W. D., AND TOMSICEK, W. J.: J. Am. Chem. Soc. **61**, 65 (1939).
(50) LARSSON, E.: Z. physik. Chem. **A159**, 306, 315 (1932); **A166**, 241 (1933); **A165**, 53 (1933).
(51) LARSSON, E., AND ADELL, B.: Z. physik. Chem. **A156**, 352 (1931).
(52) LARSSON, E., AND ADELL, B.: Z. physik. Chem. **A156**, 381 (1931); **A157**, 342 (1931).
(53) MACINNES, D. A., AND SHEDLOVSKY, T.: J. Am. Chem. Soc. **54**, 1429 (1932).
(54) MACINNES, D. A., SHEDLOVSKY, T., AND LONGSWORTH, L. G.: Chem. Rev. **13**, 29 (1933).
(55) MARTIN, A. W., AND TARTAR, H. V.: J. Am. Chem. Soc. **59**, 2672 (1937).
(56) MOELWYN-HUGHES, E. A.: Trans. Faraday Soc. **34**, 91 (1938).
(57) NIMS, L. F.: J. Am. Chem. Soc. **55**, 1946 (1933).
(58) NIMS, L. F.: J. Am. Chem. Soc. **56**, 1110 (1934).
(59) NIMS, L. F.: J. Am. Chem. Soc. **58**, 987 (1936).
(60) NIMS, L. F., AND SMITH, P. K.: J. Biol. Chem. **101**, 401 (1933).
(61) NIMS, L. F., AND SMITH, P. K.: J. Biol. Chem. **113**, 145 (1936).
(62) NOYES, A. A., AND EASTMAN, G. W.: Z. physik. Chem. **70**, 353 (1910).
(63) NOYES, A. A., AND STEWART, M. A.: J. Am. Chem. Soc. **32**, 1133 (1910).
(64) OWEN, B. B.: J. Am. Chem. Soc. **54**, 1758 (1932).
(65) OWEN, B. B.: J. Am. Chem. Soc. **55**, 1922 (1933).
(66) OWEN, B. B.: J. Am. Chem. Soc. **56**, 24 (1934).
(67) OWEN, B. B.: J. Am. Chem. Soc. **56**, 1695 (1934).
(68) OWEN, B. B.: J. Am. Chem. Soc. **56**, 2785 (1934).
(69) OWEN, B. B.: J. Am. Chem. Soc. **57**, 1526 (1935).

(70) OWEN, B. B., AND FOERING, L.: J. Am. Chem. Soc. **58**, 1575 (1936).
(71) PITZER, K. S.: J. Am. Chem. Soc. **59**, 2365 (1937).
(72) ROBERTS, E. J.: J. Am. Chem. Soc. **52**, 3877 (1930).
(73) ROBERTS, E. J.: J. Am. Chem. Soc. **56**, 878 (1934).
(74) SAXTON, B., AND LANGER, T. W.: J. Am. Chem. Soc. **55**, 3638 (1933).
(75) SHERRILL, M. S., AND NOYES, A. A.: J. Am. Chem. Soc. **48**, 1861 (1926).
(76) SMITH, P. K., TAYLOR, A. C., AND SMITH, E. B.: J. Biol. Chem. **122**, 109 (1937).
(77) WALDE, A. W.: J. Phys. Chem. **39**, 477 (1935).
(78) WRIGHT, D. D.: J. Am. Chem. Soc. **56**, 314 (1934).
(79) WYMAN, J., JR., AND MCMEEKIN, T. L.: J. Am. Chem. Soc. **55**, 908, 915 (1933).