we suppose that in largely aqueous media $\mathbf{Y}_0$ depends mainly on solvent polarity (as measured, for example, by the dielectric constant), we can extrapolate $\mathbf{Y}_0$ from ethanol–water into the still more polar systems sulfuric acid–water and perchloric acid–water. On the plot of $\mathbf{Y}_0$ *vs.* wt. % ethanol, $\mathbf{Y}_0$ approaches the origin with nearly zero slope. Therefore upon extrapolation into the systems mineral acid–water, $\mathbf{Y}_0$ remains constant at zero. Of course as the mineral acid concentration is increased and the medium becomes largely mineral acid, $\mathbf{Y}_0$ may depart noticeably from zero, and values of f_B/f_{BH} may be quite different for different structures. The actual acid–base ratios measured in solvents of around 85% sulfuric acid are correlated by one single acidity function with only moderate accuracy.[23] This would seem to confirm our preceding analysis.

To evaluate acidity functions for new solvents or charge types, one must first prove that f_B/f_{BH} is independent of acid structure. For this purpose it is necessary to study several acids of widely different m values, and our tabulations for amines and carboxylic acids can serve as a guide in designing significant experiments. Recently an attempt was made to define an acidity function $\mathbf{H}_0$ for the system ethanol–water on the basis of data for only two acids.[17] On the basis of such limited data it was not possible to decide even whether there is an acidity function,[24] and our work now shows conclusively that there is not. For the same reasons it is not possible to define[16] a function $\mathbf{H}_-$ for the carboxylic acids in the system ethanol-water. In fact, it is unlikely that $\mathbf{H}_-$ would exist even in sulfuric acid–water mixtures, for in the system ethanol–water, $\mathbf{Y}_-$ changes very rapidly with solvent composition and polarity near the origin, as the ethanol concentration approaches zero. It is interesting to note that the function $\mathbf{H}_-$ has never been reported for sulfuric acid–water mixtures even though the function $\mathbf{H}_0$ has been used for 20 years.

Acknowledgments.—We wish to thank Professors L. P. Hammett and John E. Leffler for a number of helpful discussions; the Research Corporation for a grant in support of this work; and the Atomic Energy Commission for the award of a predoctoral fellowship to Boris Gutbezahl.

TALLAHASSEE, FLORIDA

(23) See, for example: V. Gold and B. W. V. Hawes, *J. Chem. Soc.*, 2109 (1951).

(24) Reference 17, pp. 1972, 1983; see also ref. 13 for relevant data in the system dioxane–water.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE FLORIDA STATE UNIVERSITY]

The Acidity and Basicity Scale in the System Ethanol–Water. The Evaluation of Degenerate Activity Coefficients for Single Ions[1a]

BY BORIS GUTBEZAHL[1b] AND ERNEST GRUNWALD

RECEIVED APRIL 28, 1952

Acid dissociation constants in the system ethanol–water are given for carboxylic acids by (i) $pK_A - pK_A^w = \log f_H + m(HA)\ \mathbf{Y}_-$. and for anilinium and ammonium salts by (ii) $pK_A - pK_A^w = \log f_H + m(BH^+)\ \mathbf{Y}_0$. In (i) and (ii). $m(HA)$ and $m(BH^+)$ are empirical parameters characteristic of the acid. $\mathbf{Y}_-$ and $\mathbf{Y}_0$ are the corresponding activity functions.[8,9] and $\log f_H$ is a function of solvent and temperature. Values of m at 25.00° are 1.035 for acetic acid. 3.614 for aniline: and values for other acids may be calculated from these and previous correlations.[8,9] Values of $\log f_H$ for the system ethanol–water are tabulated. The empirical equations (i) and (ii) are consistent with theoretical equations involving degenerate activity coefficients only if the quantities *antilog* ($m\mathbf{Y}$) are equal to the degenerate activity coefficient ratios f_b/f_a of the bases and their conjugate acids. When either the base or the acid is a neutral molecule. the value of f for it may be measured directly. and the value of f for its ionic conjugate may then be calculated. When f has been evaluated for any one ion, values of f for other ions may be calculated by standard methods.[15] Thus there is now a method for evaluating degenerate activity coefficients for single ions. This implies, from a logical point of view, that the concept *single ion degenerate activity coefficient* is a valid one and has physical significance.

It is shown that f_H is equal to the ratio of the basicity constant (as defined by Bronsted[18]) of water to that of the ethanol–water solvent. S. As such. f_H is the equilibrium constant for the reaction SH^+ (extremely dilute. in S) + $HOH(1) = H_3O^+$ (extremely dilute. in water) + S(1). and may well be called the lyonium ion degenerate activity coefficient. With single ion degenerate activity coefficients evaluated. one can measure liquid potentials at the junction of salt solutions in two different ethanol–water solvents of different composition. As an example. the liquid potentials at the junctions: dilute solution X in ethanol–water solvent/KCl(satd., aq.) are tabulated for a number of dilute solutes X and are virtually independent of the nature of the solute.

Concordant values for the autoprotolysis constants of the ethanol–water solvents are derived from three independent potentiometric methods. Consequently values of the function $f_{OH} = K_W/K_S f_H$ are calculated. f_{OH} is equal to the ratio of the acidity constant (as defined by Brönsted[18]) of water to that of the ethanol–water solvent. and is the equilibrium constant for the reaction lyate$^-$ (extremely dilute. in S) + $HOH(1) = OH^-$ (extremely dilute. in water) + S(1). The solvent dependences of f_H and f_{OH} are consistent with predictions based on the known relative acidity and basicity of ethanol and water.

The functions f_H and f_{OH} and equations (i) and (ii) are powerful tools for the elucidation of the detailed mechanism of acid- and base-catalyzed reactions from relative reaction rates in different solvents. The methods for inferring reaction mechanism are illustrated by use of the data for the lyonium ion-catalyzed rearrangement of phenylpropenylcarbinol to its allylic isomer in the system ethanol–water. The function f_H generates an acidity scale pA. and f_{OH} generates a basicity scale pB. with the properties (i) that solutions in different solvents of equal proton activities have equal values of pA and pB. and (ii) that pA and pB reduce to pH and pOH in water. A number of good practical approximations to pA and pB are discussed. The simplest of these are $p_cA = -\log f_H - \log c_{SH^+}$. and $p_cB = -\log f_{OH} - \log c_{lyate}$.

Acidity is a chemical concept. An acidity scale must be so defined as to have chemical significance: It must measure the tendency of a solution to donate a proton to a base in a chemical equilibrium or acid-catalyzed reaction. The pA function,

---

(1) (a) This work has been supported by a grant-in-aid from the Research Corporation; (b) Atomic Energy Commission Predoctoral Fellow at Florida State University, 1951–1952.

defined by

$$pA = -\log a_+ \qquad (1)$$

(where a_+ is the proton activity) is acceptable in this sense and has the advantage of very general applicability, to solutions in aprotic solvents as well as in amphiprotic solvents.[2] It is acceptable even though it depends on the activities of single ions, quantities which cannot be measured without extrathermodynamic assumptions.[3-5]

Paralleling *p*A is the function *p*H which has been defined in various ways.[6] Perhaps the most common *p*H scales[4,6] are the concentration scale

$$p_cH = -\log c_{\text{lyonium ion}} \qquad (2)$$

and the Sörensen scale, p_sH, defined by means of the e.m.f. of reversible cells[4,6a] like (3).

$$\text{Pt-H}_2(1\ \text{atm.})/\text{solution X}/\text{KCl(aq., sat.)}/\text{Hg}_2\text{Cl}_2\text{-Hg} \qquad (3)$$

p_cH and p_sH can be measured without extrathermodynamic assumptions.

It is convenient to set up the *p*A scale such that a_+ in (1) is equal to the hydronium ion concentration in extremely dilute aqueous solutions. Then even in less extremely dilute aqueous solutions *p*A is closely approximated by either p_cH or p_sH as long as activity coefficients remain close to unity and the liquid junction potentials in cells like (3) remain nearly constant. These conditions are not satisfied by more concentrated aqueous solutions, and not at all by solutions in non-aqueous solvents.[7] Thus p_cH and p_sH cease to be acceptable measures of the acidity if one wishes to compare solutions in different solvents, and they lose much of their usefulness.

In our previous studies of the effect of solvent on the acid dissociation of carboxylic acids[8] and of ammonium and anilinium salts,[9] we were able to correlate the pK_A values in the system ethanol–water with the aid of the activity postulate.[8,10] We now combine the results of the two correlations and show that in the system ethanol–water: (i) there exists a function f_H, characteristic of the solvent; (ii) with the addition of a reasonable extrathermodynamic hypothesis, the function f_H (when combined with other, measurable quantities) generates an accurate *p*A scale.

Glossary of Symbols

c, c_a, c_b, c_{SH^+}	concentration, of acid, of conjugate base, of lyonium ion
c_H	$\equiv c_{SH^+}/X_S$ ($= c_{SH^+}$ in dilute solutions)
E	e.m.f.
E^0, E_L	standard e.m.f., liquid junction e.m.f.
f, f_a, f_b	degenerate activity coefficient, of acid, of conjugate base
f_H, f_{OH}	functions defined by equations (12) and (19)
F	Faraday charge
K	$(= c_b c_{SH^+}/c_a X_s)^a$ equilibrium constant for reaction (4)
K_A, K_B	acid, base dissociation constant
K_S, K_W	autoprotolysis constant of the solvent S, of water
$K_{S(A)}$, $K_{S(B)}$	solvent acidity, basicity constant (equation (21))
l	$(= \text{antilog}_{10}\, E_L F/2.303\, RT)$
m(HA), m(BH)	empirical parameters in equations (6)–(8)
m_-	mean value of m for acetic acid, benzoic acid, and formic acid ($= m(\text{HAc}) + 0.089)^8$
m_0	mean value of m for anilinium, *p*-toluidinium and N-methylanilinium ($= m(C_6H_5NH_3) + 0.305)^9$
p (operator)	$= -\log_{10}$; *e.g.*, $pK = -\log_{10}K$
r	variable corresponding to the radical R in the organic compound R–Z
R	gas constant/mole
s	variable corresponding to the solvent
T	temperature (°K.)
X_S	formula weight fraction of the solvent
Y_-, Y_0	activity functions (defined in ref. (8) and (9))
z	variable corresponding to the functional group Z in the organic compound R–Z
Δ (operator)	difference in value of function in solvent S and in water; *e.g.*, $\Delta E^0 = E_S - E^0_W$
ΔpK_-	mean ΔpK_A for formic acid, acetic acid and benzoic acid
ΔpK_0	mean ΔpK_A for anilinium, *p*-toluidinium and N-methylanilinium
Λ	equivalent conductance
μ_S, μ^0_W	chemical potential of the standard state in the solvent S, in water

[a] Extrapolated to infinite dilution.

The Function f_H and Degenerate Activity Coefficients for Single Ions

Functional Relationships in the Equations for ΔpK_A.—The dissociation of an organic acid in the solvent S may be represented by the general equation

$$\text{R-ZH} + \text{S} = \text{R-Z} + \text{SH}^+ \qquad (4)$$

where R–ZH is the acid, R–Z the conjugate base, and the electrical charges of R–ZH and R–Z are not indicated. The equilibrium constant K for (4) is a function of the variables s, r, z and T, corresponding to the solvent, the organic radical R, the basic functional group Z, and the temperature.

In discussing acid dissociation as represented in (4), one must distinguish between the equilibrium constant K, and the acid dissociation constant K_A. K_A is not an equilibrium constant, but is equal to K times the mass-action effect of the solvent. In the present article, it will be convenient to measure the mass-action effect of the solvent in the equilibrium (4) by its formula weight fraction, and that of the solutes by their molar concentrations. On this basis, K will be equal to K_A, both numerically and dimensionally.

A more detailed insight of the functional rela-

---

(2) See, for example: N. Bjerrum, *Chem. Rev.*, **16**, 287 (1935).

(3) E. A. Guggenheim, *J. Chem. Phys.*, **33**, 842 (1929); **34**, 1540 (1930).

(4) D. A. MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corp., New York, N. Y., pp. 258–259.

(5) J. N. Brönsted, *Z. physik. Chem.*, **A143**, 301 (1929).

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

(6a) We are using the American convention for representing cells, with the anode on the left.

(7) See, for example: L. Michaelis and M. Mizutani, *Z. physik. Chem.*, **A116**, 135 (1925).

(8) E. Grunwald and B. J. Berkowitz, THIS JOURNAL, **73**, 4939 (1951).

(9) B. Gutbezahl and E. Grunwald, *ibid.*, **75**, 559 (1953).

(10) (a) E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948); (b) E. Grunwald, *J. Phys. Colloid Chem.*, **55**, 881 (1951); (c) S. Winstein, E. Grunwald and H. W. Jones, THIS JOURNAL, **73**, 2700 (1951).

TABLE I

CALCULATION OF LOG f_H VALUES, 25.0°

Wt. % ethanol	ΔpK_- [a]	ΔpK_0 [a]	Y_- [a]	Y_0 [a]	w [b]	$\log f_- = \Delta pK_- - m_-Y_-$	$\log f_0 = \Delta pK_0 - m_0Y_0$	$\log f_H$ [c]
20.0	0.403	−0.217	0.349	−0.057	1	0.011	0.006	0.008
35.0	0.733	− .512	.596	− .136	1	.064	.021	.042
50.0	1.163	− .787	.816	− .266	1	.247	.255	.251
65.0	1.593	− .956	.924	− .379	1	.555	.529	.542
80.0	2.197	−1.044	.964	− .570	1	1.114	1.190	1.152
100.0	5.890	0.728	1.000	−1.000	0.5	4.767	4.647	4.707

[a] Values of Y_-, Y_0 from ref. (8) and (9). Values of ΔpK_- and ΔpK_0 for all solvents except 100.0% ethanol from ref. (8) and (9); the latter from ref. (12). [b] Probable errors of the data for 100.0% ethanol are approximately twice as great as those for the partly aqueous solvents. [c] Mean value of $\log f_-$ and $\log f_0$.

tionships in the equations for ΔpK ($= \Delta pK_A$) is gained if ΔpK is expressed in terms of the degenerate activity coefficients f_a and f_b of the acid and its conjugate base, and of the function f_H, as is done in the equation[11]

$$\Delta pK = \log f_H + \log f_b/f_a \qquad (5)$$

The values of $\log f_b/f_a$ depend on r, z, s and T. On the other hand, f_H is a function of s and T only. This is because f_H is the analog of a degenerate activity coefficient[11] for the function $c_H = c_{SH^+}/X_S$ and therefore depends solely on the properties of the lyonium ion and the solvent which at infinite dilution are independent of r and z.

Equation (5) may now be compared with the empirical equations for ΔpK_A. We have shown in previous articles[8,9] that the acid dissociation constants for many acids may be correlated with the aid of empirical relationships suggested by the activity postulate.[8] For example, ΔpK_A values for carboxylic acids are given by[8]

$$\Delta pK_A(\mathrm{HA}) = \Delta pK_A(\mathrm{HAc}) + [m(\mathrm{HA}) - m(\mathrm{HAc})]\, Y_- \qquad (6)$$

Since the choice of the reference substance, acetic acid (HAc), is arbitrary, equation (6) implies that there exists a function, $\Delta pK_A(\mathrm{HA}) - m(\mathrm{HA})Y_- = \Delta pK_A(\mathrm{HAc}) - m(\mathrm{HAc})\, Y_-$, independent of r and characteristic only of s, z and T. Let us call this function $\log f_-$. Then $\Delta pK_A(\mathrm{HA})$ for the carboxylic acids is given by equation (7). For the anilinium and ammonium salts one can define an analogous function, $\log f_0$, and write equation (8) for the $\Delta pK_A(\mathrm{BH})$ values.

$$\Delta pK_A(\mathrm{HA}) = \log f_- + m(\mathrm{HA})Y_- \qquad (7)$$

$$\Delta pK_A(\mathrm{BH}) = \log f_0 + m(\mathrm{BH})Y_0 \qquad (8)$$

The functional relationships in equations (7) and (8) are as follows: Y_- and Y_0 are functions of s and z; $m(\mathrm{HA})$ and $m(\mathrm{BH})$ are functions of r, z and T; and f_- and f_0 are functions of s, z and T.

One may inquire whether there is a correspondence between the functions in equation (5) and those in (7) and (8). According to the activity postulate,[8] the products $m(\mathrm{HA})Y_-$ in (7) and $m(\mathrm{BH})\cdot Y_0$ in (8) would be exactly equal to $\log f_b/f_a$ in (5). Therefore f_- and f_0 would also be equal and would both be equal to f_H. Even without the activity postulate, one may conclude from the nature of the independent variables and from the manner in which f_- and f_0 were obtained that $\log f_H$ must be contained both in $\log f_-$ and in $\log f_0$. In other words

$$\log f_- = \log f_H + \alpha_-; \text{ and } \log f_0 = \log f_H + \alpha_0 \qquad (9)$$

where α_- and α_0 are functions of s, z and T.

A New Empirical Relationship: f_- Equals f_0.—In this section we shall test whether f_- equals f_0 as required by the activity postulate. Our procedure will be to assume that the equality is correct, to treat the empirical data on this basis, and to show that the resultant fit is satisfactory.

The relevant data are summarized in Table I. The table lists the weight percentages of ethanol in the ethanol–water mixtures, the values of ΔpK_- and ΔpK_0 (as defined in the glossary of symbols), the values of Y_- and Y_0, and the appropriate statistical weights w. By using the quantities ΔpK_- and ΔpK_0 we are employing in one single treatment the entire set of accurate ΔpK_A values which we had measured previously.[8,9]

It follows from equations (7) and (8), and from the assumed equality of f_- and f_0, that

$$\Delta pK_0 - \Delta pK_- = m_0Y_0 - m_-Y_- \qquad (10)$$

Using equation (10), the quantities m_0 and m_- (which are defined in the glossary of symbols) are evaluated from the data of Table I by the method of least squares as $m_0 = 3.919$ and $m_- = 1.123$. The success of equation (10) in fitting the experimental data is tested by comparing $\log f_- = \Delta pK_- - m_-Y_-$ with the assumedly equal quantity $\log f_0 = \Delta pK_0 - m_0Y_0$. As can be seen from the last three columns of Table I, the fit is satisfactory. The probable error of fit is only 0.033 unit,[13] and this is entirely compatible with the probable errors of about 0.02–0.05 unit in the Y_0 and Y_- values. In fact, the probable error of the fit of equation (10) is hardly greater than that of equations (6)–(8) which do not involve the assumption f_- equals f_0. In the correlations according to (6)–(8), the mean probable errors of fit were 0.023 unit for the carboxylic acids,[8] and 0.018 unit for the anilinium and ammonium salts.[9] For comparison, the mean probable error of the fit of equation (7), using for $\log f_-$ the values in the last column of Table I

---

(11) f_H arises in equation (5), as follows: $K^W = a_b a_H/a_a = c_b f_b \times c_H f_H/c_a f_a = K \times f_b f_H/f_a$.

(12) H. Goldschmidt, *Z. physik. Chem.*, **99**, 116 (1921).

(13) The probable error is computed from

$$\text{p.e.} = 0.675\left[\frac{\Sigma w_i^2 d_i^2}{\Sigma w_i^2 - 8}\right]^{1/2}$$

where the d_i's are the deviations of the experimental points, and the number "8" appearing in the denominator is the number of parameters we have calculated from the data: namely, 6 values of $\log f_H$, m_- and m_0.

(which is headed log f_H), to the same ΔpK_A values for the same carboxylic acids is 0.032 unit.

On the basis of the values $m_0 = 3.919$ and $m_- = 1.123$ which best fit the data in Table I, $m(\mathrm{HAc}) = 1.035$ for acetic acid, and $m(\mathrm{C_6H_5NH_3}) = 3.614$ for anilinium ion. Values of m for other acids may be calculated from these and from the relative m values reported previously.[8,9]

The success of equation (10) is not trivial because the functions ΔpK_- and ΔpK_0, and $m_-\mathrm{Y}_-$ and $m_0\mathrm{Y}_0$, differ greatly in their dependence on solvent composition, both with respect to magnitude and with respect to sign. The actual accuracy of the equal valued parameters log f_- and log f_0 (which we have collected in the last column of Table I) is somewhat less than the probable error of fit of equation (10). We estimate probable errors of about 0.05 unit (and no greater than 0.10 unit) for the values in the ethanol–water mixtures, and of about 0.10 unit (but no greater than 0.20 unit) in 100% ethanol.

The Relationship of f_- and f_0 to f_H. The Evaluation of f_H.—In the preceding section we have shown that the values of f_- are equal to those of f_0 within the limits of accuracy of the other quantities in equations (7) and (8). It follows that the quantities α_- and α_0 in (9) are equal, at least within a probable error of 0.03 unit. In this section we shall attempt to evaluate α_- and α_0, and thus log f_H.

Our first method is based on a study of functions of s and z. In principle, α is a function of s, z and T. In fact, α_- is equal to α_0. This implies that α is virtually independent of z, for the two types of acids—carboxylic acids and anilinium and ammonium salts—have been purposely selected so as to make z as different as possible. The acids have different charge types and different basic atoms.

All other known functional relationships with respect to s are very different for these two values of z. We have already pointed to the lack of similarity of the functions ΔpK_- and ΔpK_0, and of $m_-\mathrm{Y}_-$ and $m_0\mathrm{Y}_0$, as ethanol is added to the solvent. We wish to stress that these functions differ greatly not only in curvature and concavity, but especially in magnitude, and usually in sign.

Since all other functional relationships with respect to s are strikingly different for the two values of z, it is reasonable to expect that α_- must also be very different from α_0. With the observed difference between α_- and α_0 being negligibly small, α_- and α_0 must then themselves be negligibly small and, to a good approximation, equal to zero. It follows that $f_- = f_0 = f_H$.

The same conclusion may be reached by an alternative argument. The empirical equations (7), (8) and (10) were tested because they were suggested by the activity postulate. This postulate was not an arbitrarily selected relationship, but *a priori* there was a rather good probability that it would correctly predict the values of log f_b/f_a in equation (5). The activity postulate was first made as a result of our correlations of specific solvolysis rates in hydroxylic solvents.[10] The lawfulness which we discovered among solvolysis rate constants extended over wide ranges of s and r and was equivalent to a relationship among degenerate activity coefficients. This relationship appeared to be of a type that might have general applicability in hydroxylic solvents. And in fact, when the relationship was written in more general form and used as an activity postulate, it could accommodate[10a] the data on acid dissociation of substituted anilinium salts in systems such as sulfuric acid–water which Hammett and coworkers had previously correlated[14] with the acidity function H_0.

The activity postulate imposes some very characteristic and stringent requirements on the functional relationships in the equations for ΔpK_A. There is the requirement that the quantities log f_b/f_a in (5) be expressible as products of a function m, independent of s, and of a function **Y**, independent of r. These requirements have been satisfied in the empirical equations (7) and (8). There is the further requirement—also stringent—that the terms log f_- and log f_0 in (7) and (8) be equal. This has also been realized. Thus all the necessary conditions for the validity of the activity postulate in the present systems have been satisfied.

It is highly improbable that *all* the necessary conditions for the validity of the activity postulate could be satisfied unless the postulate itself were valid. This belief is strengthened further by the fact that the activity postulate is valid also in other, similar systems.[10] If we therefore infer that the activity postulate is valid here, we must conclude that $\log f_b/f_a = m\mathrm{Y}$, and that $f_- = f_0 = f_H$.

Evaluation of Degenerate Activity Coefficients for Single Ions in the System Ethanol–Water.—As a result of the identification of the $m\mathrm{Y}$ terms in (7) and (8) with log f_b/f_a in (5), it is possible to calculate the degenerate activity coefficients of single ions. For example, let us calculate the degenerate activity coefficient for ammonium ion in 100% ethanol. Using solubility data in water[15] and ethanol,[16] $f_{\mathrm{NH_3}}$ is calculated to be 7.17. The ratio $f_{\mathrm{NH_3}}/f_{\mathrm{NH_4^+}} = \mathrm{antilog}_{10}\ m(\mathrm{NH_4})\mathrm{Y}_0$ and is calculated to be 3.31×10^{-4} from the Y_0 and m values reported in this and the preceding paper.[9] Therefore $f_{\mathrm{NH_4^+}} = 2.17 \times 10^4$ in 100% ethanol. Values of $f_{\mathrm{NH_4^+}}$ for the other ethanol–water solvents may be obtained by analogous methods.

It is well known that degenerate activity coefficients for *all* ions may be evaluated by standard thermodynamic methods as soon as the value for *any one* is available.[17] Therefore the values of $f_{\mathrm{NH_4^+}}$ which we have just obtained are sufficient to make determinate all other single ion degenerate activity coefficients in the system ethanol–water.

We wish to review briefly the logical significance of these single ion degenerate activity coefficients. A careful analysis of this problem has already been made by Brönsted[5] whose conclusions we accept.

---

[14] L. P. Hammett and A. J. Deyrup, THIS JOURNAL, **54**, 2721 (1932); L. P. Hammett and M. A. Paul, *ibid.*, **56**, 827 (1934).

[15] F. E. C. Scheffer and H. J. de Wijs, *Rec. trav. chim.*, **44**, 654 (1925).

[16] I. M. Barclay and J. A. V. Butler, *Trans. Faraday Soc.*, **34**, 1445 (1938).

[17] See, for example: J. N. Brönsted, A. Delbanco and K. Volqvartz, *Z. physik. Chem.*, **A162**, 128 (1932).

The degenerate activity coefficient f is quite generally defined for both neutral and ionic solutes by

$$RT \ln f = \mu^0_S - \mu^0_W \tag{11}$$

where the standard chemical potential $\mu^0 = \mu - RT \ln cy$. In other words, when the given solute is at equal chemical potential in the medium S and in water, the distribution ratio c_W/c_S approaches the limit f at infinite dilution. For an electrically neutral component, equality of chemical potential implies that there is phase equilibrium with respect to the component. There are no further restrictions regarding the activities of the other components or regarding the electrical states of S and of water. When the component is an ion, equality of chemical potential no longer implies that there is phase equilibrium unless the two phases are at equal electrical potential.[3,5] Since it is not possible to measure the difference in the electrical potentials of two different media,[3,5] it is not possible to evaluate f for single ions from phase equilibrium data, and extrathermodynamic methods such as we have used must be resorted to. It is nevertheless possible to *define* f in terms of phase equilibrium if one adopts a convention regarding the zero point of electrical potential of the two phases. Brönsted has suggested[5] that the electrical potential of a given isolated homogeneous phase be set equal to zero when the phase is completely uncharged, that is, when the total charge due to all the anions in the phase is exactly equal to the total charge due to all the cations. This convention makes μ equal to the *electrochemical* potential[3,5] of the ion in the completely uncharged phase. In order to define μ also for non-zero values of the electrical potential, it is sufficient to regard μ as independent of the electrical potential. This may be done without inconsistency with thermodynamics, for the functions of μ, such as the equilibrium and rate constants of ionic reactions, are independent of the electrical state of the medium.

On the basis of this definition, f for a single ion is equal to the limit of the distribution ratio c_W/c_S at infinite dilution when the ion is distributed between the completely uncharged and electrically isolated media S and water. Except for this added restriction regarding the electrical states of the two media, f for an ion is therefore completely analogous to f for a neutral component.

The question whether a given set of single ion activity coefficients has been evaluated accurately is not important in those problems where the approach is macroscopic or thermodynamic. When these problems involve ion activities, the equations always contain the activity coefficients of more than one ion. If an error has been made in the extrathermodynamic evaluation of the activity coefficient for one of the ions, this error will be exactly cancelled by compensating errors in the other activity coefficients.[3] On the other hand, there are many problems involving ion activities which require a microscopic or mechanistic approach, and in the solution of these problems the accuracy of the extrathermodynamic evaluation is of the utmost importance. Conversely, when these problems have already been solved by independent methods, they may be used to confirm the accuracy of the extrathermodynamic evaluation. In subsequent sections we shall carry out several such confirmatory tests for our set of single ion degenerate activity coefficients.

The Chemical Significance of the f_H Values.—In the discussion of equation (5), we have described f_H as the cofactor of c_H, *formally* analogous to a degenerate activity coefficient.[11] To visualize the chemical significance of f_H, we express K_A/K_A^w (which is equal to K/K^w for equilibrium (4)) in terms of solvent basicity constants as defined by Brönsted,[18] namely

$$K_A/K_A^w = (f_a/f_b)(K_{S(B)}/K_{W(B)}) \tag{12}$$

Comparison of equation (12) with (5) leads to the recognition that

$$f_H = (K_{W(B)}/K_{S(B)}) \tag{13}$$

Thus f_H turns out to be simply a ratio of solvent basicity constants—another example of the great unifying power of the Brönsted definitions[18] in the quantitative treatment of proton transfer phenomena.

According to equation (13), f_H is the equilibrium constant for the reaction

$$\begin{aligned} &SH^+ \text{ (at infinite dilution in S)} + HOH \text{ (liquid)} = \\ &\qquad H_3O^+ \text{ (at infinite dilution in water)} + S\text{(liquid)} \end{aligned}$$

Therefore in very dilute solutions in the solvent S and in water, the proton activities are equal when the lyonium ion concentrations are in the ratio $1{:}f_H$. It seems logical to call f_H the *lyonium ion degenerate activity coefficient*, a name we have used before.[8]

f_H values may be used to obtain the degenerate activity coefficients of other ions. For example, the standard electromotive force of the cell, $Pt-H_2/HCl$(c, in S or in water)/$AgCl-Ag$, varies with solvent according to

$$\Delta E_0 = -(RT/F) \ln f_H f_{Cl^-} \tag{14}$$

and may be used to calculate f_{Cl^-}. Using the available data[6a] for 100% ethanol[19] and water[20] at 25.0°, $E_0(EtOH) = -0.0882$ v., $E_0(W) = 0.2215$ v., $\log f_H = 4.707$ (Table I), and therefore $f_{Cl^-} = 3.38$.

A Further Test of Validity.—From the values for $f_{NH_4^+}$ and f_{Cl^-} obtained in the preceding sections we calculate 2.70×10^2 for the mean degenerate activity coefficient of ammonium chloride in 100% ethanol. This quantity may also be calculated from the solubilities and mean molar activity coefficients of ammonium chloride in water and ethanol according to

$$f_{\pm} = [cy_{\pm}](NH_4Cl\text{, sat., aq.})/[cy_{\pm}](NH_4Cl\text{, sat., ethanol})$$

Accurate determinations give the values 5.70 and 0.789 for the concentration and mean molar activity coefficient of ammonium chloride in the saturated aqueous solution.[21] The solubility of ammonium

---

(18) J. N. Brönsted, *Z. physik. Chem.*, **A163**, 52 (1934); *Chem. Revs.*, **5**, 231 (1928).

(19) J. W. Woolcock and H. Hartley, *Phil. Mag.*, [7] **5**, 1133 (1928).

(20) H. H. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943, pp. 34–37, 316–325, 336, 537.

(21) J. N. Pearce and G. C. Pumplin, THIS JOURNAL, **59**, 1219 (1937).

chloride in ethanol is 0.091 ± 0.002 vol. formal,[22] but the molar activity coefficient has not been measured. Therefore we have approximated it by using the value 0.241 measured for hydrogen chloride at the same concentration.[19] The error introduced in this way is not likely to exceed a few per cent. The two salts have the same anion and structurally similar cations. Their conductance curves in ethanol are very similar. Particularly their conductometric ion pair dissociation constants, which are a good index of the non-colligative terms in the expression for the activity coefficient, are very nearly equal.[23]

From these data we calculate the value 2.05 × 10^2 for the mean degenerate activity coefficient of ammonium chloride in ethanol. This is in satisfactory agreement with the result, 2.70 × 10^2, of the previous independent calculation. The discrepancy between the two values, amounting to 0.12 logarithmic unit, is well accounted for by experimental errors and errors inherent in the other assumptions.

The close agreement of the results of the two calculations indicates more than the internal consistency of our single ion degenerate activity coefficients. While the second calculation depended very much on the thermodynamic properties of ammonium chloride in ethanol, the first was quite independent of data for ammonium chloride or other ammonium salts measured directly in ethanol. In the calculation of $f_{NH_4^+}$, the parameter $m(NH_4)$ was calculated from acid dissociation constants in solvents other than 100% ethanol, and Y_0 for 100% ethanol was calculated from data for acids not including ammonium ion. The calculation of f_{Cl^-} involved the value of f_H which was obtained according to equation (10) and its corollaries from data independent of the acid dissociation constants of ammonium ion. Thus the first calculation is really a prediction, and its success confirms the validity of our correlations.

Applications

The Calculation of Liquid Junction Potentials.—From a knowledge of f_H or of other single ion degenerate activity coefficients it is possible to calculate the potential in suitable cells at the junction of solutions in different solvents. For example, the liquid junction potential of the cell[6a]

$$\text{Pt–H}_2\text{(1 atm.)/solution X in ethanol–water solvent}/E_L/\text{KCl (sat., aq.)/Hg}_2\text{Cl}_2\text{–Hg} \qquad (3')$$

is given by

$$E_L = (RT/F) \ln l = E - E^0_{\text{calomel}} + (RT/F) \ln (c_{SH^+} y_{SH^+} f_H) \qquad (15)$$

The cell (3′) has been used extensively. The e.m.f. seems to be reproducible to better than 2 mv. in independent experiments[7,24–26] and remains constant for many hours.[26b] When the solution X is one of hydrogen chloride at low concentration, y_{SH^+} in (15) can be estimated with sufficient accuracy from the Debye–Hückel limiting law,[20] all other quantities on the right-hand side of (15) are measurable or tabulated, and E_L may be calculated. When the solution X contains a weak acid in equilibrium with its conjugate base, it is customary to measure an apparent dissociation constant K_A' defined[7,24,25] by

$$\log K_A' = \frac{F}{2.303\ RT} (E^0_{\text{calomel}} - E) + \log \frac{c_b}{c_a}$$

K_A' is related to K_A by

$$pK_A - pK_A' = -\log l + \log f_H + \log (y_a/y_b) \qquad (16)$$

For dilute solutions, log (y_a/y_b) may again be estimated from the Debye–Hückel limiting law,[20] all other quantities in (16) are measurable or tabulated, and log l (or E_L) can be calculated.

In cells of the type (3′), the liquid junction potentials E_L for various dilute solutions X in a given ethanol–water mixture ought to be quite constant. When the solute concentrations in solution X are small compared to that of potassium chloride in the saturated aqueous solution, electric current is carried across the junction almost exclusively by the potassium or chloride ions which are present in large excess in the volume element joining the two liquid phases. Under these conditions, E_L would depend mainly on the composition of the ethanol–water solvent and on certain properties of the potassium and chloride ions, notably their mobilities and activity coefficients.[27]

In practice, E_L values are quite constant for a given solvent over wide ranges of solute structure. Some relevant data, calculated from equations (15) and (16), are summarized in Table II. The solute concentrations used in these experiments have been low enough so that molar activity coefficients could be approximated by the Debye–Hückel limiting law. Column 1 of Table II lists the solvent compositions. Columns 2 to 6 contain values of log l from five independent sources, calculated from data for solutions X (see cell 3′) in which the solutes are hydrogen chloride, anilines and their hydrochlorides, and carboxylic acids and their sodium salts. Column 7 lists the mean values of log l, and their mean deviations. Column 8 lists the corresponding values of E_L. It is seen that the mean deviations of the log l values range from 0.02 to 0.04 unit, the maximum deviation of any two values for the entire table being 0.15 unit. These deviations are consistent with the precision measures of the source data. The *accuracy* of the log l values is somewhat less than their precision, being limited by the accuracy of log f_H. We estimate probable errors of the order of 0.05 unit for log l, and of 0.03 unit for the sum (log l − log f_H) which is not limited by the accuracy of log f_H.

The constancy of the log l values in Table II over such a wide range of solute structure may be interpreted in two ways. It may be taken to confirm the theoretical arguments leading to its

---

[22] Own measurements in 99.98% ethanol. Herz and Kuhn (*Z. anorg. Chem.*, **58**, 159 (1908); **60**, 152 (1908)) have reported 0.099 vol. *f*. for the solubility in slightly moist ethanol. Their solvent contained about 0.6% water judging by its density.

[23] I. Bezman and F. H. Verhoek, THIS JOURNAL, **67**, 1330 (1945).

[24] M. Mizutani, *Z. physik. Chem.*, **A116**, 350 (1925).

[25] H. Baggesgaard-Rasmussen and F. Reimers, *Dansk. Tidsskr. Farm.*, **7**, 164, 225 (1933).

[26] (a) G. Schwarzenbach, *Helv. Chim. Acta*, **16**, 522 (1933); (b) G. Schwarzenbach and H. Egli, *ibid.*, **17**, 1176 (1934); (c) G. Schwarzenbach and A. Epprecht, *ibid.*, **19**, 493 (1936).

[27] See, for example: M. Planck, *Wied. Ann.*, **40**, 561 (1890); ref. (4), chapter 13.

TABLE II

LIQUID JUNCTION POTENTIALS IN CELL (3′). 25.0°

Wt. % ethanol	log l Source A[a]	Source B[a]	Source C[a]	Source D[a]	Source E[a]	log l (av.)	E_L (mv.)
20.0	−0.057	−0.047	−0.003	+0.025	−0.034	−0.023 ± 0.027	− 1.4
35.0	+ .075	+ .139	+ .095	+ .115	+ .122	+ .109 ± .020	+ 6.4
50.0	+ .357	+ .508	+ .400	+ .408	+ .430	+ .421 ± .039	+24.9
65.0	+ .727	+ .764	+ .693	+ .732	+ .760	+ .735 ± .021	+43.5
80.0	+1.259	+1.233	+1.272	+1.242	+1.312	+1.264 ± .023	+74.8
100.0	.....	.....	.....	(+2.35)	.....	(+2.35)	(+139)

[a] Source A—mean pK_A and pK_A' values for formic acid. acetic acid and benzoic acid; ref. (8). (7). (24). Source B—mean pK_A and pK_A' values for anilinium and N-methylanilinium; ref. (9) and (24). Source C—weighted average pK_A and pK_A' values for propiónic acid (1). malonic acid ($^1/_2$). succinic acid ($^1/_2$) and glutaric acid ($^1/_2$); statistical weights in approximate inverse proportion to experimental error; ref. (8) and (26a,c). Source D—data for hydrogen chloride; ref. (26a). Source E—mean pK_A and pK_A' values for formic acid. acetic acid and chloroacetic acid; ref. (8) and (25).

prediction. Conversely, it may be taken to indicate the internal consistency of the five different sets of experimental data, and thus greatly strengthen our faith in their absolute accuracy.

Autoprotolysis Constants and Acidity Constants of the Ethanol-Water Solvents.—One of the important physical constants of an amphiprotic solvent is its autoprolysis constant.[18] This constant is of particular interest in the present work because it is equal to the product of the solvent acidity and basicity constant[18,28]

$$K_S = \kappa_{S(A)}\kappa_{S(B)} \qquad (17)$$

Having evaluated the lyonium ion degenerate activity coefficient f_H, we now define the lyate ion degenerate activity coefficient f_{OH} by

$$pK_S - pK_W = \log f_H + \log f_{OH} \qquad (18)$$

It then follows from (13), (17) and (18) that

$$f_{OH} = \kappa_{W(A)}/\kappa_{S(A)} \qquad (19)$$

Equation (19) implies that in very dilute solutions in S and in water the proton activities are equal when the lyate ion concentrations are in the ratio $1:f_{OH}$.

In order to obtain a valid set of pK_S values and, subsequently, of f_{OH} values, we shall compare the results of three independent potentiometric methods for the measurement of pK_S. None of the methods is entirely free from non-thermodynamic assumptions, and therefore none of the three sets—if taken by itself—is entirely acceptable. Although each of the three potentiometric methods involves different non-thermodynamic assumptions, the resultant sets of pK_S values are in fairly close agreement. Therefore the possible criticisms of any one method are largely eliminated, and there is considerable confidence in the final results.

Method A.—The e.m.f. of cell (3′) has been measured at 20.0° in a number of ethanol–water mixtures with solution X containing either dilute (*ca.* 0.01 *N*) hydrogen chloride or sodium lyate.[26a] Since we have demonstrated that E_L in cell (3′) is very nearly constant for all dilute solutions X, pK_S values at 20.0° may be calculated at once by standard methods. The results have been corrected to 25.0° with sufficient accuracy by using the same temperature coefficient as measured in water.[29] Values of pK_S at rounded weight percentages of ethanol have been obtained by interpolation from a large-scale plot and are listed in Table III.

TABLE III

VALUES OF THE AUTOPROTOLYSIS CONSTANTS, OF f_H, AND OF f_{OH}, FOR THE SYSTEM ETHANOL–WATER, 25.0°

Wt. % Ethanol	pK_S method A	pK_S method B	$E_{(a)}$ (mv.) method C	pK_S method C	pK_S (av.)	log f_H	log f_{OH}
0.0	...	...	35.1	...	14.00[a]	0.00	0.00
20.0	14.30	...	35.7	14.36	14.33	.01	.32
35.0	14.59	...	34.2	14.55	14.57	.04	.53
50.0	14.89	14.89	30.7	14.86	14.88	.25	.63
65.0	15.22	15.37	23.8	15.28	15.29	.54	.75
80.0	15.71	16.14	17.0	15.88	15.91	1.15	.76
100.0	...	19.5	..	...	19.5	4.71	.8

[a] Reference (29).

Method B.—The autoprotolysis constants at 25.0° are calculated from the acid and base dissociation constants of a conjugate acid–base couple,[30] *i.e.*, $K_S = K_AK_B$. K_A and K_B are both obtained by a differential potentiometric method which is relatively free from non-thermodynamic assumptions.[30] However, the accuracy of the results suffers somewhat because of the need to evaluate a derivative, and because of the poor buffering capacity of the test solutions when K_A and K_B are as small as in these experiments. The pK_S values at rounded weight percentages of ethanol listed in Table III have been obtained by interpolation on a large-scale plot.

Method C.—The e.m.f. of cell (20) has been measured at 25.0° in a number of ethanol–water mixtures.[31] The autoprotolysis

$$\text{Pt-H}_2/\text{HCl (0.01 } N)^{(a)}/\text{LiCl (0.01 } N)^{(b)}/\text{NaOH (0.01 } N)/\text{Pt-H}_2 \qquad (20)$$

All solutions in ethanol–water solvent

constants may be calculated by standard methods when the liquid junction potentials at (a) and (b) in cell (20) are known and when suitable values of molar activity coefficients are available. The latter may be estimated with sufficient accuracy in 0.01 *N* solutions from the Debye–Hückel limiting law, and the former are approximated by[27,31]

---

(28) In equations (17)–(19) we use molar concentrations to measure the mass-action effect of lyonium and lyate ion, and K_S to measure that of the solvent.

(29) Reference 20, p. 581. The temperature coefficients of pK_W are nearly equal to those of pK_S in dioxane–water mixtures (*ibid.*) and in methanol (N. Bjerrum, A. Unmack and L. Zechmeister, *C. A.*, **19**, 3196 (1925)).

(30) S. Kilpi and H. Warsila, *Z. physik. Chem.*, **A177**, 427 (1936).

(31) R. Löwenherz, *ibid.*, **A20**, 283 (1896).

$$E_{(a)} = (RT/F) \ln (\Lambda_{HCl}/\Lambda_{LiCl}) \text{ and}$$
$$E_{(b)} = (RT/F) \ln (\Lambda_{LiOH}/\Lambda_{NaCl})$$

The equivalent conductances at 25.0° of 0.01 N solutions of hydrogen chloride and lithium chloride at the rounded weight percentages of ethanol listed in Table III may be deduced with sufficient accuracy by interpolation between published data,[32,33] and $E_{(a)}$ calculated. The results are included in Table III. Equivalent conductances for lithium hydroxide (or lyate) and sodium chloride are available in water[20] and ethanol,[34] but apparently not for ethanol–water mixtures—neither directly nor indirectly *via* data for other salts and the law of independent ion migration. Fortunately $E_{(b)}$ is small; it is 16.1 mv. in water, −3.0 mv. in ethanol; and it must have intermediate values at intermediate compositions. In order to calculate pK_S values for the ethanol–water solvents, we have assumed a linear relationship between $E_{(b)}$ and the weight per cent. ethanol. The error due to this assumption is not likely to exceed 0.10 pK unit. The resulting pK_S values are included in Table III.

The autoprotolysis constant of ethanol has been measured potentiometrically by a number of workers.[30,35–37] The measurement is very sensitive to the presence of even traces of water in the solvent, and the various results are somewhat discordant. The pK_S values 18.93, reported by Macfarlane and Hartley,[37] and 19.14, reported by Danner,[35] are probably too low, one factor being that these workers may have overestimated the required values of molar activity coefficients. The values 19.34, reported by Larsson,[36] and 19.52, reported by Kilpi and Warsila,[30] are in fair agreement, and at least the latter result is not debited with many non-thermodynamic assumptions. We have used the value 19.5 for pK_S of ethanol in preparing Table III.

Averaged values of pK_S, of $\log f_H$, and of $\log f_{OH}$ are given in the last three columns of Table III. f_H and f_{OH} are related to the basicity and acidity constant of the solvent by equations (13) and (20).

The acidity and basicity constant of a solvent depends both on its chemical properties, *i.e.*, its tendency to lose and receive a proton, and on its physical, mostly electrical, properties, such as the dielectric constant.[2,18] To examine these relationships in greater detail, we write

$$K_{S(A)} = c_{\text{lyate}}\, a_+ / X_S \text{ and } K_{S(B)} = c_{\text{lyonium}}/X_S a_+ \quad (21)$$

We note that the acid ionization of the solvent generates charge, and hence $K_{S(A)}$ must be sensitive both to the electrical and to the chemical properties of the solvent. On the other hand, the reaction of the solvent as a base conserves charge, and $K_{S(B)}$ is consequently quite independent of electrical properties and varies mainly with chemical properties.

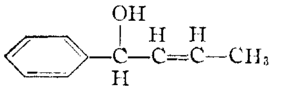
Returning again to the properties of ethanol–water mixtures, there is evidence of long standing that ethanol is a weaker base than water.[23,38] It can be inferred that ethanol is a stronger acid than water because methanol is a stronger acid than water.[39] Ethanol has a lower dielectric constant than water and is less favorable to reactions in which charge is generated.

The values of $\log f_H$ and of $\log f_{OH}$ listed in Table III accurately reflect these solvent properties. As ethanol is added to water, $\log f_H$ remains quite constant in spite of a lowered dielectric constant until enough has been added to decrease appreciably the basicity of the medium. $\operatorname{Log} f_H$ then increases, as expected, and the rate of increase becomes very great near 100% ethanol where the lyonium ion changes from hydronium ion to ethyloxonium ion.[23,38] On the other hand, f_{OH} increases at first, reflecting the effect of the lowered dielectric constant on acidity, until enough of the more strongly acidic ethanol has been added to partially offset the electrical effect. The rate of increase of log f_{OH} then levels off to almost zero, indicating that the electrical and chemical effects nearly cancel. It is gratifying to note that the leveling-off of f_{OH} begins at the same solvent composition, *ca.* 40% ethanol, where f_H begins to increase.

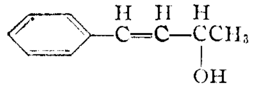
Acid- and Base-catalyzed Reactions.—The functions f_H and f_{OH} can sometimes be used to advantage to solve questions of mechanism for acid- and base-catalyzed reactions. Many acid- and base-catalyzed reactions proceed by a two-step mechanism[18,40]: The first step is a rapid and reversible pre-equilibrium involving the substrate, its conjugate acid or base, and lyonium or lyate ion. The second step is a slow and rate-determining reaction of the conjugate acid or base of the substrate. The mechanism of this second step is of crucial interest, and much insight may be gained from the knowledge of the solvent dependence of its specific rate. On the basis of our work, some semi-quantitative deductions may be made which are often decisive for mechanism.

To illustrate our methods, we choose as an example the specific lyonium ion-catalyzed rearrangement of phenylpropenylcarbinol (22) to its allylic isomer (23).[41] The kinetics is second order,

(22)



(23)



first order each with respect to alcohol and lyonium ion.[41a,b] The second-order rate constants have been measured for 0.1 N solutions of hydrogen chloride in solvents containing 40–100 vol. % ethanol. and also for 0.01 N solutions in some

---

[32] I. Kablukoff, *Z. physik. Chem.*, **A4**, 429 (1889).

[33] L. C. Connell, R. T. Hamilton and J. A. V. Butler, *Proc. Roy. Soc.* (*London*), **A147**, 418 (1934).

[34] M. Barak and H. Hartley, *Z. physik. Chem.*, **A165**, 272 (1933).

[35] P. S. Danner, This Journal, **44**, 2832 (1922).

[36] E. Larsson, dissertation, Lund, 1924; quoted by ref. (30).

[37] A. Macfarlane and H. Hartley, *Phil. Mag.*, [7] **13**, 425 (1931).

[38] (a) H. Goldschmidt, *Z. physik. Chem.*, **89**, 129 (1914); (b) H. Thomas and L. Marum, *ibid.*, **143**, 191 (1929); (c) A. J. Deyrup, This Journal, **56**, 60 (1934); (d) E. A. Braude and E. S. Stern, *J. Chem. Soc.*, 1976 (1948).

[39] A. Unmack, *Z. physik. Chem.*, **A129**, 349 (1927).

[40] See, for example: L. Zucker and L. P. Hammett, This Journal, **61**, 2791 (1939).

[41] (a) E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 436 (1944); (b) E. A. Braude, E. R. H. Jones and E. S. Stern, *ibid.*, 396 (1946); (c) E. A. Braude and E. S. Stern, *ibid.*, 1982 (1948).

solvents.[41b,c] The rearrangement is most probably represented by the scheme

$$\mathrm{ROH} + \mathrm{H}^+ \overset{K_A^{-1}}{\rightleftarrows} \mathrm{ROH_2}^+ \text{ (rapid. reversible)} \quad (1)$$

$$\mathrm{ROH_2}^+ \xrightarrow[\text{slow}]{k} \mathrm{R'OH_2}^+ \quad (2)$$

and the intimate mechanism of the rearrangement step 2 is of particular interest.

Neglecting temporarily the effect of solvent change on the molar activity coefficients, the observed second-order rate constants may be written simply as

$$\log k_2 = \log k/K_A = \log k/K_A{}^w + \log f_H + m(\mathrm{ROH_2})\mathrm{Y_0} \quad (24)$$

According to (24), a plot of $[\log k_2 - \log f_H]$ *vs.* $\mathrm{Y_0}$ is linear if k is independent of solvent, and in general is curved if k varies with solvent. In this way, the solvent dependence of k may be determined.

Interpolated values[41c] of $\log k_2$ at rounded weight percentages of ethanol are listed in Table IV. The equation

$$\log k_2 = -0.278 + \log f_H + 4.823\ \mathrm{Y_0} \quad (25)$$

TABLE IV

CORRELATION OF THE SPECIFIC RATES FOR THE ACID-CATALYZED REARRANGEMENT OF PHENYLPROPENYLCARBINOL 30.0°

Wt. % ethanol	$-\log k_2$ (sec.$^{-1}$ M^{-1}) obsd.	$-\mathrm{Y_0}$	$-\log k_2$ (sec.$^{-1}$ M^{-1}) calcd., eq. (25)
35.0	0.856	0.136	0.822
50.0	1.285	.266	1.310
65.0	1.652	.379	1.564
80.0	1.862	.570	1.875
100.0	0.379	1.000	0.394

has been calculated from these data and fits with a probable error of only 0.039 unit. There is no systematic curvature. Therefore k is independent of solvent, at least within the limits of sensitivity of this sort of a treatment. The treatment will not detect small trends of k with solvent, but decisively rules out gross changes of k, particularly in the region near 100% ethanol where they would be most likely to occur.

Equation (24) is approximate because no terms have been included for molar activity coefficients. In the several solvents where measurements have also been made for 0.01 N acid,[41b] the second-order rate constants are about 10% less than for 0.1 N acid.[41c] Thus the term containing the molar activity coefficients seems to be near unity and fairly constant for all solvents. In the least squares treatment of the data, the term is absorbed in the intercept, −0.278, which is therefore not quite equal to $\log k/K_A{}^w$. Only one solvent, 70 vol. % ethanol (65 wt. %), is exceptional. The specific rate for 0.1 N acid is 7.5% *lower* than for 0.01 N acid. At the same time, the calculated value of $\log k_2$ for 65% ethanol is the only one in the entire Table IV that deviates appreciably from the observed value. An increase in k_2 of 17.5% for this solvent would reduce the deviation to almost zero.[42] Thus a rigorous treatment, allowing for molar activity coefficients, would fit even better than equation (25).

Because of the success of equation (25) it is improbable that step 2 proceeds (as has sometimes been visualized[41b]) by a mechanism such as $\mathrm{S_N2'}$ in which the solvent acts as a nucleophilic agent.[43] Other mechanisms, such as $\mathrm{S_N1}$ or *internal return*,[44] are still possible.

Solvation Energies of Ions.—From the degenerate activity coefficients one can calculate, by virtue of equation (11), the standard partial molar free energies of solvation relative to water for single ions. Work along these lines is in progress in this Laboratory, and only one point is worth mentioning at this time.

The degenerate activity coefficient of ammonium ion in ethanol, 2.17×10^4, is much greater than that, 3.3_8, of chloride ion. This indicates either that the mechanisms of solvation for the two ions are quite different, or that, regardless of mechanism, the solvation number of ammonium ion is much greater than that of chloride ion. There is previous independent evidence which has been interpreted in the same way.[45,46] Thus our degenerate activity coefficients are again consistent with previous evidence, indicating again their probable correctness.

A Practical Acidity and Basicity Scale for the System Ethanol–Water.—In the previous sections we have evaluated the functions f_H and f_{OH}, and developed the relevant equations, notably (1), (2), (13), (15), (17)–(19) and (21), which are required to establish a practical acidity or basicity scale for the system ethanol–water. The acidity and basicity scales must have the properties (i) that they reduce to pH and pOH in water; and (ii) that solutions of equal acidity or basicity in different solvents have the same proton activities. In establishing a practical scale, we desist from being thermodynamically rigorous, and we do not claim for our scale an accuracy in excess of a few hundredths of a unit. For example, we shall neglect the difference between $p\mathrm{H} = -\log c_{\mathrm{SH^+}} y_{\mathrm{SH^+}}$, as ideally defined, and such practical approximations[6] as p_cH (equation 2).

In order that the acidity scale pA, defined by equation (1), reduce to pH in water, it is necessary to set $\mathrm{K_{W(B)}} = 1$. Then

$$p\mathrm{A} = -\log f_H - \log c_{\mathrm{SH^+}} y_{\mathrm{SH^+}} \quad (26)$$

$$\approx p_c\mathrm{A} \equiv -\log f_H + p_c\mathrm{H} \quad (27)$$

for dilute solutions. Similarly the basicity scale pB will reduce to pOH in water if

$$p\mathrm{B} = -\log f_{OH} - \log c_{\mathrm{lyate}} y_{\mathrm{lyate}} \quad (28)$$

$$\approx p_c\mathrm{B} \equiv -\log f_{OH} - \log c_{\mathrm{lyate}} \quad (29)$$

---

(42) This unusual behavior of k_2 in 65% ethanol need not be real. There may be determinate error, or there may be a misprint in the journal.

(43) R. E. Kepner, S. Winstein and W. G. Young, THIS JOURNAL, **71**, 115 (1949).

(44) J. D. Roberts, W. G. Young and S. Winstein, *ibid.*, **64**, 2157 (1942); W. G. Young, S. Winstein and H. L. Goering, *ibid.*, **73**, 1958 (1951).

(45) See, for example: P. M. Gross, *Chem. Revs.*, **13**, 91 (1933), especially p. 99.

(46) J. N. Sugden, *J. Chem. Soc.*, 174 (1926).

for dilute solutions. From these definitions it follows that for any solution, in any solvent

$$pA + pB = pK_W \qquad (30)$$

The scales p_cA and p_cB, defined by (27) and (29), are useful practical scales in many cases. Perhaps the most generally applicable scales are, however, the functions p_sA and p_sB which are defined in terms of the e.m.f. of cells like (3′). For example, from cell (3′)

$$p_sA = (E - E^0_{\text{calomel}} - E_L)F/2.303\ RT \qquad (31)$$

where E^0_{calomel} is 0.2455 v. at 25.0°,[47] and E_L is given in Table II. p_sB is calculated from p_sA using equation (30). If a cell other than (3′) is used, an unknown pA may be measured if the cell is first calibrated[20] with a dilute solution of known pA in the same solvent. For the calibration one may use perhaps a dilute solution of hydrogen chloride, or perhaps a buffer solution of a suitable weak acid and its conjugate base. Accurate pK_A values are available for this purpose for a great many weak acids in the system ethanol–water.[8,9]

Acknowledgments.—It is a pleasure to acknowledge helpful discussions with Drs. J. E. Leffler and M. G. Alder of this University, and with Dr. L. P. Hammett of Columbia University. We wish to thank the Research Corporation for a grant-in-aid of this work, and the A.E.C. for the award of a fellowship to B. G.

TALLAHASSEE, FLA.

[47] H. Riehm, *Z. physik. Chem.*, **A160**, 1 (1932); M. Duboux and G. Pièce, *Helv. Chim. Acta*, **23**, 152 (1940).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TASMANIA]

Urea Formaldehyde Kinetic Studies. III. Polarographic Studies in Dilute Solution

BY LLOYD E. SMYTHE

RECEIVED JULY 21, 1952

The reaction between (a) urea, (b) N-methylurea, (c) N-ethylurea and formaldehyde has been studied in dilute solution at pH 7.15 using the polarographic method for following the concentration of unreacted formaldehyde. This method is given in some detail since it has been found suitable for following the course of industrially used condensations. The diffusion current in the selected buffer, although reduced, was adequate in giving smooth polarographic steps few of which exhibited maxima. Thus the use of maximum suppressors was avoided. The reactions were found to be second order and rate constants and energies of activation have been evaluated. Differences have been observed in the reaction of urea with formaldehyde as compared with the simple N-alkyl ureas and formaldehyde. It is suggested that in the case of alkyl ureas some effective resonance stabilization is lost and the effect becomes more pronounced in dilute solution resulting in increased reactivity. Hydration of both the urea and formaldehyde is appreciable in the region of pH 7; the reactions reaching a certain stage and being unable to proceed further. The effect of acid or alkaline condensing agents in dilute solution would be initially to break down forces of hydration and in the case of alkaline solutions the reaction is reversible. The initial rapid reaction previously observed becomes less important with increasing dilution and the significance of this is discussed.

Part II of this series[1] indicated that dilution of reactants exerted a considerable influence on the nature of the initial reaction between urea and formaldehyde. It was also evident that the analytical method for the estimation of formaldehyde[2] was subject to some errors when working with dilute solutions.

A study of the reaction in dilute solution using urea and N-alkyl ureas was commended. The polarographic method appeared to be the most suitable in this case and Crowe and Lynch[3] had successfully used it employing 0.05 N lithium hydroxide and buffers giving supporting electrolyte pH values from 8.6–12.7. In all cases the reaction was shown to be reversible and equilibrium constants were evaluated. Earlier observations[4] had indicated that while most alkaline condensing agents are effective for the formation of methylol compounds there was evidence of some hydrolysis of the condensation product, equilibrium evidently being attained, particularly at pH values greater then 9.0. In this study it was desirable that the pH of the supporting electrolyte be maintained as closely as possible to 7, so as not to influence materially the forward or reverse reactions. The effect of phosphate buffers on the reaction has been studied[1] and preliminary studies using different supporting electrolytes indicated that Sørensen buffer of seven parts by volume of $M/15$ Na_2HPO_4 and three parts by volume of $M/15$ KH_2PO_4 giving a pH of 7.15 at 25°, provided a suitable supporting electrolyte.

Experimental

The polarographic measurements were made with a Tinsley ink recording polarograph (V722/1) employing d.c. amplification of the current passing through the solution in the polarographic cell. The recorder unit was a moving coil d.c. pen type milliameter, the standard speed being 1 inch per minute corresponding to a voltage change of 0.5 v. The "capillary constant" K was 23.82 using 0.1 M CH_2O in Sørensen buffer containing dissolved air: applied voltage −1.65 v., head of mercury 501 mm., drop time 2.52 sec., temperature 25°. The radius of the capillary orifice[5] ρ determined in 0.2 M KCl at 25° using an open circuit was 25 microns.

With Sørensen buffer supporting electrolyte containing dissolved air, the half-wave potentials were −1.65 and −1.73 v. *vs.* the mercury pool electrode and *vs.* the saturated calomel electrode, respectively. Concentration of formaldehyde within the range 0.01–0.10 M exhibited this half-wave potential but concentrations of 0.10–0.50 M resulted in a shift to a slightly more negative potential. Figure 1 shows the relation between the diffusion current in microamperes and concentration expressed as molarity. Sensitivities corresponding to full scale deflection on the recording chart were selected to give the largest possible step. Ac-

---

[1] L. E. Smythe, THIS JOURNAL, **74**, 2713 (1952).

[2] L. E. Smythe, *J. Phys. Colloid Chem.*, **51**, 396 (1947).

[3] G. A. Crowe and C. C. Lynch, THIS JOURNAL, **70**, 3795 (1948); **71**, 3731 (1949); **72**, 3622 (1950).

[4] L. E. Smythe, unpublished work.

[5] O. H. Müller, "The Polarographic Method of Analysis," J. Chem. Education, Easton, Pa., pp. 182-190, 1951.