

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

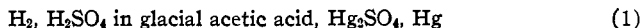
ACTIVITY COEFFICIENTS OF SULFURIC ACID IN ANHYDROUS ACETIC ACID

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In a recent paper Hutchison and Chandlee² have reported measurements on the cell without transfer



corresponding to the process $\text{H}_2(\text{g}) + \text{Hg}_2\text{SO}_4(\text{s}) = \text{H}_2\text{SO}_4(\text{m}) + 2\text{Hg}(\text{l})$ (2 faradays) at 25° for molalities of sulfuric acid ranging from $m = 0.8715$ to $m = 0.0025$. These measurements are particularly valuable for, as the authors point out, they are not burdened with the uncertainties of liquid junction potentials, and the logical objections to individual ion activities which are inherent in data obtained from cells with transference, a criticism that may be raised against previous e. m. f. measurements in glacial acetic acid.

In this paper we shall present a modified interpretation of their data and show that they conform to the Debye-Hückel theory over a wider concentration range than does the original interpretation.

To evaluate E° , for the computation of the mean activity coefficients of sulfuric acid, Hutchison and Chandlee consider sulfuric acid as a ternary electrolyte ($\nu = 3$) dissociating into 2 H^+ and SO_4^- ions, and employ a two parameter equation; namely, the simple form of the Debye-Hückel theory (first approximation of the Poisson-Boltzmann equation) in combination with the linear term added by Hückel to account for changes in the dielectric constant, as a control on the extrapolation to infinite dilution. Since the dielectric constants of conducting solutions are not susceptible to experimental measurement and in aqueous solutions where the various attempts at measurement have led to widely different and often absurd results,³ the arbitrary parameter B involved in the Hückel extension cannot be regarded at the present time other than as a purely empirical correction term, we shall therefore restrict our computations to the region where the better theoretically founded parameter " a ," corresponding to the distance of closest approach of the ions, involved in the original form of the theory suffices as an explanation.

Our treatment differs in that we shall consider sulfuric acid when dissolved in glacial acetic acid as a binary electrolyte ($\nu = 2$) dissociating into H^+ and HSO_4^- ions. Owing to the high degree of acidity of glacial acetic acid, any secondary dissociation of the HSO_4^- ion into SO_4^{--} and

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² Hutchison and Chandlee, *THIS JOURNAL*, **53**, 2881 (1931).

³ Harned, *ibid.*, **48**, 326 (1926).

H⁺ ions would be completely repressed. In addition we shall take into account the higher terms, (III) and (V), of the Gronwall, La Mer and Sandved⁴ solution of the Poisson-Boltzmann equation which were neglected in Hutchison and Chandlee's treatment, namely

$$\begin{aligned}
 -\log_{10} f = & 19.63 \left(\frac{z^2}{a}\right) \frac{x}{1+x} - 320.7 \left(\frac{z^2}{a}\right)^3 \cdot 10^3 \left[\frac{1}{2} X_3(x) - 2Y_3(x) \right] \\
 & \text{(I)} \qquad \qquad \qquad \text{III} \\
 & - 26,200 \left(\frac{z^2}{a}\right)^5 \cdot 10^5 \left[\frac{1}{2} X_5(x) - 4Y_5(x) \right] \qquad \text{(2)} \\
 & \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \text{V}
 \end{aligned}$$

In Table I are given the observed e. m. f.'s, E , corresponding to the molalities m . The other quantities are defined as follows

$$\begin{aligned}
 E^{\circ'} &= E + \frac{\nu RT}{nF} \log m = E + 0.05915 \log m \\
 &= E^{\circ} - 0.05915 \log f
 \end{aligned} \qquad (3)$$

$$\kappa = \sqrt{\frac{4\pi N e^2}{1000 k T D} \sum n_i z_i^2} = 1.1734 \times 10^8 \sqrt{c} \qquad (4)$$

when we substitute D (acetic acid) = 6.165 and the numerical values of the universal constants. It is important to emphasize that the assump-

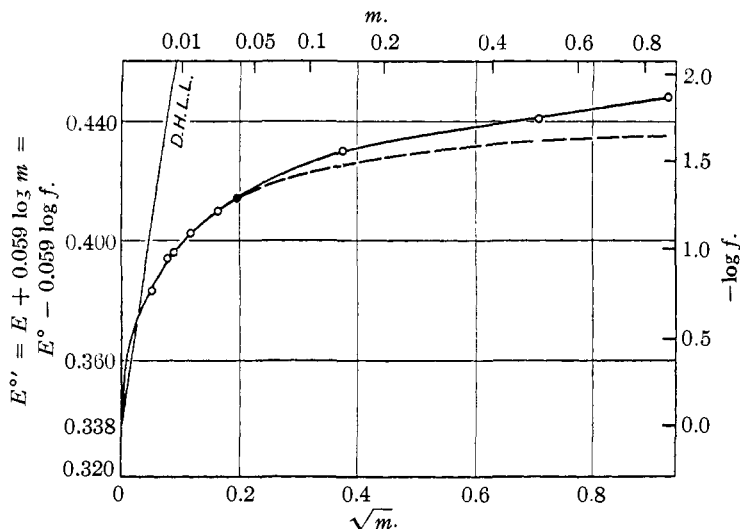


Fig. 1.—Heavy curve—Experimental: $E^{\circ'} = E + 0.05915 \log m$.
Dotted curve—Theory: Gronwall, La Mer and Sandved; "a" = 11 Å.;
 $E^{\circ'} = E^{\circ} - 0.05915 \log f = 0.338 + 0.05915$ [Eq. (2)].

tion that $\nu = 2$ leads to an entirely different set of values for $E^{\circ'}$ and consequently for E° than those employed by Hutchison and Chandlee. Similarly, their values of κ are reduced by the factor $\sqrt{3}$ and the limiting

⁴ Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928).

slope of $\log f$ against \sqrt{m} by the factor $2\sqrt{3}$ by this assumption. Another advantage is that we can employ the symmetrical solution of the Poisson-Boltzmann equation as given by Gronwall, La Mer and Sandved⁴ and not be obliged to carry out the tedious computations involved in the unsymmetrical case.⁵

TABLE I
COMPUTATION OF E° FOR $\nu = 2$

No.	m	E	E°	ϵ	$\sqrt{\epsilon}$	$10^{-3} \kappa$
1	0.002461	0.537	0.3827	0.002567	0.05067	0.0595
2	.006053	.525	.3938	.006315	.07947	.0933
3	.007730	.521	.3961	.008063	.08979	.1054
4	.01377	.512	.4019	.01436	.1198	.1406
5	.02662	.5035	.4104	.02773	.1665	.1954
6	.03796	.498	.4140	.03954	.1988	.2333
7	.1437	.480	.4302	.1490	.3860	.4529
8	.5014	.459	.4413	.5133	.7164	.8406
9	.8715	.452	.4483	.8770	.9365	1.0989

Table II gives the computations for " a " = 11 Å., which value of " a " gives the most constant and therefore the most acceptable value of E° .⁶

The computed values of E° for this and other values of " a " are plotted in Fig. 2. It is noteworthy that a one-parameter function yields a value of E° which is constant to within the limits of experimental error (≈ 0.001 volt) for the six determinations extending over the concentration range $m = 0.0025$ to $m = 0.038$, whereas under the assumption $\nu = 3$ two parameters are required to account for these data. A small empirical correction term of the order of $0.02 m$ is sufficient to account for the deviation of the last three points from $E^\circ = 0.338$.

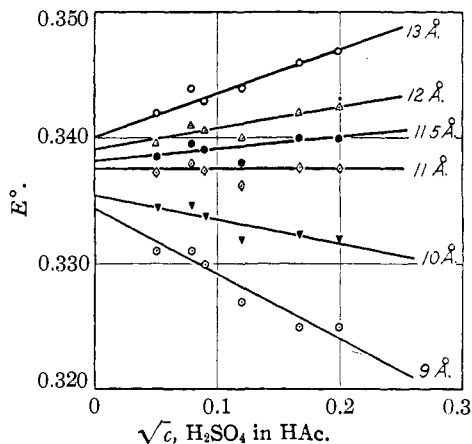


Fig. 2.

From recent measurements on the solubility of univalent salts in glacial acetic acid, Seward and Hamblet⁷ have shown that " a " is equal to 8.5 to 9.5 Å. and that it is unnecessary in dilute solution to introduce a term for change of dielectric constant, which is in agreement with our conclusions.

⁵ La Mer, Gronwall and Greiff, *J. Phys. Chem.*, **35**, 2245 (1931).

⁶ For details concerning this computation see La Mer and Parks, *THIS JOURNAL*, **53**, 2040 (1931); Cowperthwaite and La Mer, *ibid.*, **53**, 4333 (1931).

⁷ Seward and Hamblet, *ibid.*, **54**, 554 (1932).

TABLE II
COMPUTATION OF E° FOR " a " = 11 Å.

No.	$x = ka$	I	III	V	$-\log f$	$\frac{-0.05915}{\log f}$	E°
1	0.6541	+0.706	-0.088	+0.026	+0.768	0.0454	0.337
2	1.0258	.904	-.057	.018	.943	.0558	.338
3	1.1594	.958	-.048	.014	.992	.0587	.337
4	1.5466	1.084	-.028	.003	1.109	.0656	.336
5	2.1494	1.218	-.013	..	1.231	.0728	.338
6	2.5663	1.284	-.007	..	1.291	.0764	.338
7	4.9819	1.487	1.487	.0880	.342
8	9.2466	1.611	1.611	.0953	.346
9	12.0879	1.649	1.469	.0975	.351

Summary

The e. m. f. measurements of Hutchison and Chandlee on the activity coefficient of sulfuric acid in glacial acetic acid can be accounted for on the basis of the Gronwall, La Mer and Sandved extension of the Debye-Hückel theory on the assumption that sulfuric acid behaves as a binary electrolyte in this solvent with an " a " value equal to 11 Å., for the concentration range $m = 0.0025$ to 0.038 .

$E^\circ = 0.338$ volt for the cell H_2, H_2SO_4 in glacial acetic acid, Hg_2SO_4, Hg .
NEW YORK, N. Y.

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MOLECULAR ROTATION IN THE SOLID STATE. THE VARIATION OF THE CRYSTAL STRUCTURE OF AMMONIUM NITRATE WITH TEMPERATURE

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The phenomenon of molecular rotation in the solid state, first recognized by L. Pauling,¹ is proving of wide occurrence. In sodium nitrate² the picking up of rotational energy by the nitrate groups takes place over an extended temperature interval and is accompanied by *gradual* changes in such properties as coherent scattering of x-rays, heat capacity and specific volume. Pauling interpreted the *gradual* transitions shown by methane, hydrogen bromide, hydrogen iodide and the ammonium halides as accompanying molecular rotation. He also suggested that the *polymorphic* transitions shown by nitrogen (35.4°K.), oxygen (43.75°K.) and hydrogen chloride (93.36°K.) are accompanied by the excitation of molecular rotation.

The several gradual transitions shown by hydrogen bromide and hydro-

¹ L. Pauling, *Phys. Rev.*, **36**, 430 (1930).

² F. C. Kracek, E. Posnjak, S. B. Hendricks, *THIS JOURNAL*, **53**, 3339 (1931).