

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE PENNSYLVANIA STATE COLLEGE]

ACTIVITY COEFFICIENTS OF SULFURIC ACID IN ANHYDROUS ACETIC ACID

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In a recent series of papers entitled "Superacid Solutions"¹ acid-base relationships in glacial acetic acid solutions have been studied. These authors reached the conclusion that acids dissolved in this solvent possess a high acidity when compared with similar aqueous solutions. The explanation of this relationship is based on the modern conception of acids and bases expressed by Brönsted.²

The conclusions of Hall and co-workers¹ are based in part on the nature of titration curves for anhydro bases with acids in glacial acetic acid solution. The potential difference between a saturated chloranil electrode in the solution of the base and an aqueous saturated potassium chloride calomel half-cell joined to the acetic acid solution by means of a stoppered salt bridge containing a saturated solution of lithium chloride in acetic acid was measured. This potential changed with the addition of acid solutions to the base and a plot of the potentials measured against the quantity of acid added showed clearly the course of the neutralization and its end-point.

Since the reference potential of the saturated chloranil electrode is independent of the solvent, a knowledge of the liquid junction potentials involved would allow such a cell to be used as a measure of the familiar P_H of the solution. The authors have considered the sum of these potentials to be constant in the various solutions measured and have estimated it. From these values they have calculated values of the acidities of the various solutions in terms of a quantity $P_H^{(HAc)}$ comparable to the usual P_H . These values for acid solutions were generally negative, indicating a greater acidity than is possessed for aqueous solutions of the same acids.

This work suggested the desirability of obtaining further information regarding the activity of acids in a solvent of the high acid character possessed by acetic acid.

The measurement of cells without transference furnishes at once a method of obtaining values for the activity or the mean ionic activity coefficients for a solute with no uncertainty beyond the accuracy with which the measurements are made. The activities so obtained are expressed in terms of a standard reference state for the solvent concerned and are not directly comparable to activities in water solution.

¹ Hall and Conant, *THIS JOURNAL*, **49**, 3047 (1927); Conant and Hall, *ibid.*, **49**, 3062 (1927); Hall and Werner, *ibid.*, **50**, 2367 (1928); Conant and Werner, *ibid.*, **52**, 4436 (1930).

² Brönsted, *Rec. trav. chim.*, **42**, 718 (1923).

In the present work the potential differences between a hydrogen electrode and a mercury-mercurous sulfate electrode in solutions of sulfuric acid in anhydrous acetic acid from 0.0025 to 0.9 molal in strength have been measured. The reference potential for this cell in acetic acid has been obtained by an extrapolation method based on the Debye-Hückel theory of strong electrolytes and the applicability of this theory to a solvent of a very low dielectric constant has been demonstrated.

Experimental

Preparation of Materials.—Glacial acetic acid of U. S. P. grade was purified by refluxing for ten hours with an excess of chromium trioxide to remove any easily oxidizable material. The acid was distilled from the solid residue and then carefully fractionated in a packed column rectifying still similar to that described by Marshall.³ A reflux ratio of one to ten was used. The packing of the column was of glass tubing of small diameter cut in such lengths as to give cylinders of equal height and diameter. The packing in the column extended five feet. All of the operations were conducted in all-glass apparatus and at all times the acid was protected from atmospheric moisture by calcium chloride tubes. The main fraction melted at 16.55°, corresponding to an acid of 99.975% purity on the reasonable assumption that the freezing point lowering was due to water.⁴

Anhydrous sulfuric acid was made by mixing concentrated acid with fuming acid, both of Baker's analyzed grade, as described by Kendall and Carpenter.⁵ It froze at 10.3°.

The mercurous sulfate was of the best grade obtainable. Mercury of a C. P. grade was further purified by washing in dilute nitric acid and distilling in a current of air as recommended by Hulett and Minchin.⁶ Electrolytic hydrogen, dried with phosphorus pentoxide, was used for the hydrogen electrodes.

The solutions were made by adding to a weighed amount of the pure acetic acid the desired amount of sulfuric acid from a weight buret. In the calculations of the molalities of the solutions the necessary corrections for vacuum weights were made. The densities of five of these solutions were determined and the equation $d_4^{25} = 1.043 + 0.062m$ was found to express the relationship between density and molality up to 0.87 molal. This equation was used in calculating the concentrations from the molalities.

The potentials listed are the average of readings taken on two cells prepared at different times. Three pairs of platinum electrodes were used in each cell, thus giving a total of twelve readings at each concentration. When the cell solution was saturated with hydrogen equilibrium was reached almost immediately. The reproducibility of these measurements was about 2 millivolts. In the case of solutions 1 and 9 hydrogen was allowed to bubble slowly for five hours through the cell with no change in potential greater than 4 millivolts. In the case of other cells the constancy of potential for one hour was assumed sufficient test that equilibrium had been reached. The potentials were independent of the rate of hydrogen flow after the solution had been thoroughly saturated with hydrogen.

All electromotive force measurements were made with a Leeds and Northrup type K potentiometer by the null method. The potentiometer calibrations were checked in this Laboratory and were found to be as indicated within the limits demanded by the experiments. A saturated Weston standard cell was used as a reference e. m. f. It was

³ Marshall, *Ind. Eng. Chem.*, **20**, 1379 (1928).

⁴ De Visser, *Rec. trav. chim.*, **12**, 101 (1893).

⁵ Kendall and Carpenter, *THIS JOURNAL*, **36**, 2498 (1914).

⁶ Hulett and Minchin, *Phys. Rev.*, **21**, 388 (1905).

checked from time to time during the course of the experiments against two other cells of the same type recently calibrated at the Bureau of Standards. In place of the usual galvanometer a Compton quadrant electrometer was used as an indicating instrument. The instrument was used with negative electrostatic control as described by Compton and Compton.⁷ Its sensitivity was 3000 mm. per volt. All of the apparatus was completely shielded, the lead wires by lead pipe, and the potentiometer, standard cells, and working battery in specially constructed metal boxes. The electrometer was suspended in a Julius suspension so as to free it from possible mechanical disturbances and the shielding completely eliminated accidental electrical effects. Switches were placed near the potentiometer so that the electrical stirring device as well as the heating system of the thermostat could be disconnected at the time readings were being taken. The lead wires were of No. 18 copper wire. Platinum wires were fused to the ends of the wires used to make connections by means of dipping into mercury. This prevented the possible contamination of the mercury.

The thermostat was maintained at a temperature of $25 \pm 0.01^\circ$. The cells were placed in a copper tank, filled with oil, suspended in the thermostat water.

The cells were of the H type, Fig. 1, similar to that described by Noyes and Ellis⁸ and were made by connecting two Pyrex test-tubes by means of a short, about 8-cm., piece of tubing of 7-mm. diameter. A piece of the same tubing was sealed to the bottom of one of the tubes and bent so that it became parallel to the tube. This tube then became the mercury-mercurous sulfate half-cell, and connection was made to it by means of a platinum wire dipping into the mercury. In the second tube was placed a stopper through which were inserted two hydrogen electrodes with mercury contacts and tubes for the inlet and outlet of hydrogen. In some of the preliminary experiments cells of different types were used, some with a stopcock on the cross arm. No difference in potential was noted, so that the simple type described was used in all of the final work. Hydrogen was saturated with acetic acid before entering the cell by bubbling it through a wash bottle, immersed in the thermostat, containing the solution being measured. The outlet tube was protected from the atmosphere by an acetic acid seal.

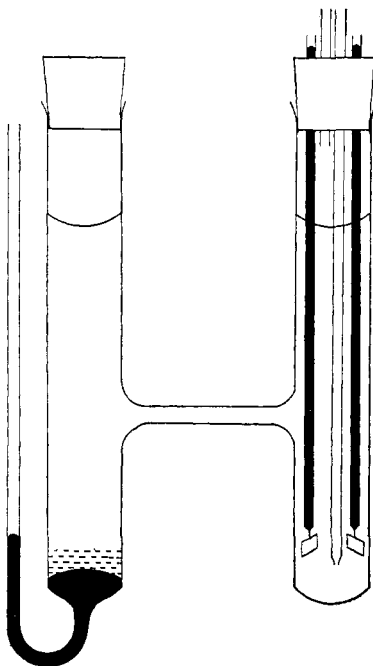


Fig. 1.—The cell.

Data and Calculations

In order to evaluate the activity of the mean ionic activity coefficient of sulfuric acid in the solutions, we may use the equations of Lewis and Randall⁹

⁷ Compton and Compton, *Phys. Rev.*, **14**, 85 (1919).

⁸ Noyes and Ellis, *THIS JOURNAL*, **39**, 2532 (1917).

⁹ Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances." McGraw-Hill Book Co., Inc., New York, 1923, p. 355.

$$E = E^\circ - \frac{RT}{2F} \ln a_2 \quad (1)$$

$$E = E^\circ - \frac{3RT}{2F} \ln (\gamma m^{4/3}) \quad (2)$$

Before a_2 or γ can be evaluated, a value for E° must be determined. Transforming (2) and introducing common logarithms

$$2.303 \times \frac{3RT}{2F} \log \gamma = E^\circ - \left(E + 2.303 \times \frac{3RT}{2F} \log m^{4/3} \right) \quad (3)$$

If the quantity in the parentheses, E°' , is plotted against some function of m , extrapolation of the curve to $m = 0$ gives at once the value of E° . The

TABLE I
EXPERIMENTAL DATA

Solution	m	$(m)^{1/3}$	E	E°
1	0.002461	0.1350	0.537	0.323
2	.006053	.1823	.525	.346
3	.007730	.1977	.521	.351
4	.01377	.2397	.512	.365
5	.02662	.2986	.5035	.382
6	.03796	.3361	.498	.390
7	.1437	.5238	.480	.423
8	.5014	.7944	.460	.451
9	.8715	.9552	.452	.465

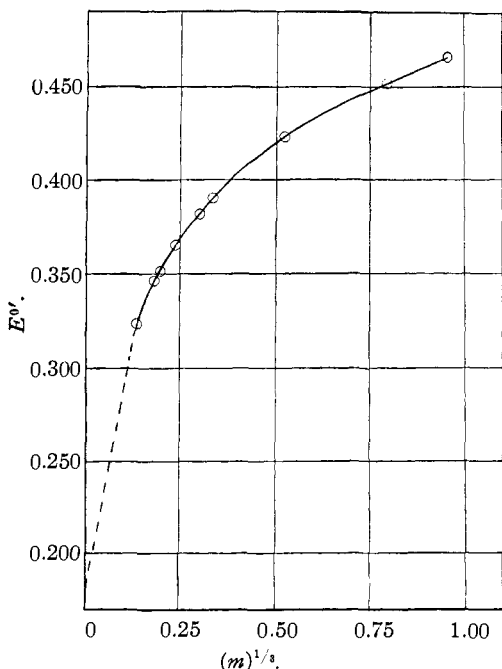


Fig. 2.

data are given in Table I and in Fig. 2 values of E°' have been plotted against $(m)^{1/3}$. Inspection of the graph shows that the curve is approaching a straight line with, however, such a steep slope that a slight error in the choice of its slope would make a large one in the value of E° obtained by simple extrapolation. Solutions less concentrated than 0.0025 molal gave erratic potentials, so that no significance could be attached to them.

The Debye-Hückel¹⁰ theory, however, allows an evaluation with reasonable security of activity coefficients in very dilute solutions. The fundamental equation may be written

¹⁰ Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

$$-\ln f = \frac{A \epsilon^2 z_1 z_2 K}{2DRT(1 + Kb)} \quad (4)$$

$$K^2 = \frac{8\pi \epsilon^2 A^2 \mu}{1000 DRT} \quad (5)$$

The values for the universal constants were taken from the "International Critical Tables," that of the dielectric constant, $D = 6.165$, from the recent work of Smyth.¹¹ Substituting the numerical values for the constants

$$K = 1.1734 \times 10^8 \sqrt{\mu} \quad (6)$$

Transforming to common logarithms and noting that in the very dilute solutions $f = \gamma$ where γ is the mean ionic activity coefficient based on molality

$$-\log \gamma = \frac{23.033 z_1 z_2 \sqrt{\mu}}{1 + 1.1734 \times 10^8 b \sqrt{\mu}} \quad (7)$$

which for an electrolyte of the 2-1 type in acetic acid can be written

$$-\log \gamma = \frac{79.79 \sqrt{c}}{1 + 2.0325 \times 10^8 b \sqrt{c}} \quad (8)$$

This equation has been modified by Hückel¹² for use in more concentrated solutions by the introduction of a third term to allow for consideration of the changing dielectric constant of the pure solvent brought about by the introduction of solute. For sulfuric acid solutions in acetic acid the equation may be written

$$-\log \gamma = \frac{79.79 \sqrt{c}}{1 + 2.0325 \times 10^8 b \sqrt{c}} - \beta c + \log(1 + 0.18m) \quad (9)$$

The last term is necessary in concentrated solutions because of the transformation from an activity coefficient based on mole fraction to one based on molality.

Equation (2) may be written

$$E = E^\circ - 0.08872 \log(\gamma m^{4^{1/3}}) \quad (10)$$

$$\log \gamma = -\frac{E}{0.08872} - \log m + \left(\frac{E^\circ}{0.08872} - \log 4^{1/3} \right) \quad (11)$$

and denoting the quantity in parentheses by K

$$-\log \gamma + K = \frac{E}{0.08872} + \log m \quad (12)$$

The constants b and β of equation (9) were evaluated by the method proposed by Hückel¹² on page 123 of his article. Such modification of the equations given as was necessary for a 2-1 type electrolyte was made. The values found were $b = 1.5 \times 10^{-7}$ and $\beta = -0.35$.

If the data of Table II are substituted in equation (12) and values of $-\log \gamma + K$ are plotted against the half-power of the concentration, the

¹¹ Smyth, *THIS JOURNAL*, **52**, 1825 (1930).

¹² Hückel, *Physik. Z.*, **26**, 93 (1925).

TABLE II
 EXPERIMENTAL DATA

Solution	m	c	$(c)^{1/2}$	B	$-\text{Log } \gamma + K$	$(-\text{Log } \gamma + K) - K$
1	0.002461	0.002567	0.05067	0.537	3.44	1.60
2	.006053	.006315	.07947	.525	3.71	1.87
3	.007730	.008063	.08980	.521	3.76	1.92
4	.01377	.01436	.1198	.512	3.91	2.07
5	.02662	.02773	.1665	.5035	4.10	2.26
6	.03796	.03954	.1989	.498	4.19	2.35
7	.1437	.1490	.3860	.480	4.57	2.73
8	.5014	.5133	.7165	.459	4.89	3.05
9	.8715	.8770	.9370	.452	5.04	3.20

curve should be of the same nature as that of equation (9). In Fig. 3 the full curve is that of equation (9). The circles represent values of $(-\log \gamma + K) - K$, taking K as 1.84.

It is of interest to see just how much influence the various terms of equation (9) have on values of $-\log \gamma$. In the extremely dilute solutions

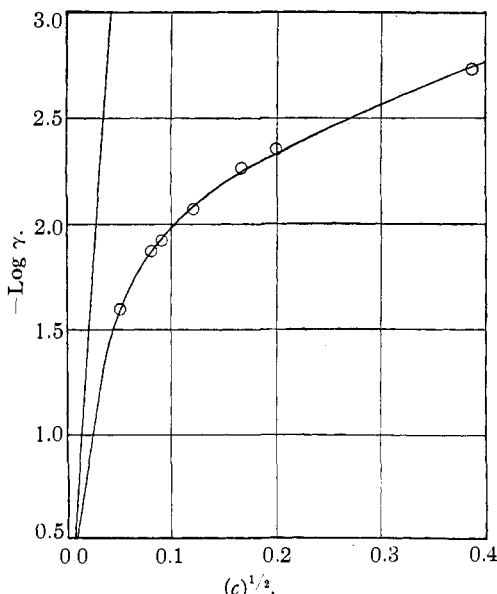


Fig. 3.

the slope of the curve should be 79.79, represented by the straight line of Fig. 3. It is not surprising that even at the very low concentrations measured this slope is not reached since the dielectric constant of acetic acid has such a small value. Introduction of the ion diameter term, however, gives a coincidence of the four experimental points with the curve up to 0.014 molal. The addition of the second term includes three additional points up to 0.15 molal. The more concentrated solutions depart from the theoretical curve. In Table III are listed the values for the terms of the Hückel equation, $-\log \gamma$ calculated

from this equation and $-\log \gamma$ experimentally determined from the value of $(-\log \gamma + K) - K$ taking K as 1.84.

A comparison of the values used for the arbitrary constants with those chosen by other workers may be of interest. The value chosen for b , the average ion diameter in the solution, is somewhat larger than is generally used in aqueous solutions but is of the same order as values used by other

TABLE III

Solution	(1st term)	EXPERIMENTAL DATA			
		$-B\theta c$	$\text{Log}(1 + 0.18m)$	$-\text{Log } \gamma$ (calcd.)	$-\text{Log } \gamma$ (exp.)
1	1.59	0.01		1.60	1.60
2	1.86	.01		1.87	1.87
3	1.92	.02		1.94	1.92
4	2.06	.03		2.09	2.07
5	2.19	.06		2.25	2.26
6	2.25	.08		2.33	2.35
7	2.42	.31	0.01	2.74	2.73
8	2.51	1.08	.04	3.63	3.05
9	2.53	1.84	.06	4.43	3.20

workers in acetic acid solutions. Conant and Werner,¹ in applying the Debye-Hückel equation to data for sulfuric acid-anhydro base buffer solutions in acetic acid used values of 1.3×10^{-7} and 1.24×10^{-7} for b , with, however, a slightly different limiting slope because of a different value for the dielectric constant. Webb¹³ in studying the freezing points of acetic acid solutions of salts used for b , in the case of lithium bromide, 7.1×10^{-8} , for sodium bromide, 6.8×10^{-8} , and for sodium acetate, 6.2×10^{-8} . He apparently used a still different value for the dielectric constant.

The large values for b in acetic acid solutions might be accounted for by considering the ions solvated in all solvents, and since the acetic acid molecules are probably larger than water molecules, an increased diameter would be expected. In general the ion diameter b is larger than the diameter of ions in the crystal lattice.

The value of B in aqueous solutions is ordinarily a small positive number. However, Webb¹³ found that his data were in accord with an equation of the type of (9) only when B was a negative number. Thus for lithium iodide b is taken as 6.75×10^{-8} and B as -1.38 . The sign of the constant could be explained on the assumption that the dielectric constants of the solutions are greater than that of the pure solvent. Walden and Ulich¹⁴ and Walden, Ulich and Werner¹⁵ have found that with many organic solvents the dielectric constant is increased on the addition of electrolytes.

From the value of 1.84 assigned to K a value for E° of 0.181 volt can be calculated. Then for solutions of sulfuric acid in acetic acid at 25.0° may be written the equation

$$E = 0.181 - 0.08872 \log (\gamma m^{4^{1/2}}) \quad (13)$$

from which activity coefficients can be calculated at any molality measured.

Summary

A convenient method for the preparation of large quantities of anhydrous acetic acid of a high grade has been found.

¹³ Webb, THIS JOURNAL, 48, 2266 (1926).

¹⁴ Walden and Ulich, Z. physik. Chem., 110, 43 (1924).

¹⁵ Walden, Ulich and Werner, *ibid.*, 116, 261 (1925).

A general equation for the calculation of activity coefficients of sulfuric acid in glacial acetic acid solutions has been developed.

It has been shown that an equation of the type proposed by Hückel as a modification of the Debye-Hückel theory of strong electrolytes is applicable in a solvent of very low dielectric constant.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE DIPOLE MOMENT OF SEMI-POLAR BONDS

By JOHN DEVRIES AND WORTH H. RODEBUSH

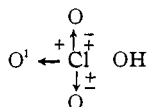
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The term semi-polar bond has been used to designate a shared electron bond in which both electrons are contributed by one atom. This term has been used in the absence of a more suitable designation without much idea as to its fitness since it has not been known with certainty whether any considerable degree of polarity is characteristic of this bond. Two common examples of this bond are ammonium chloride and perchloric acid.



In the case of the ammonium chloride the identity of the semi-polar bond is completely lost. In the perchloric acid the strength of the acid may be explained by assuming a considerable degree of polarity in the semi-polar bonds thus



Any other explanation of the strength of perchloric acid seems to be barred, since double bonds are out of the question.

It is impossible to determine the dipole moment of the semi-polar bonds in the above-mentioned molecules for obvious reasons. Recently, however, Professor Shriner¹ of this Laboratory has synthesized some organic sulfur compounds which contain semi-polar bonds. Professor Shriner has kindly furnished us with samples of these compounds for measurement of the electrostatic moment. The compounds were diphenyl sulfoxide, diphenyl sulfones and homologs. The electronic structures of the sulfoxide and sulfone are



¹ Shriner, Struck and Jorison, *THIS JOURNAL*, **52**, 2060 (1930).