the anion. The comparatively few instances of the hydration of an ammonium salt, however, may be taken as illustrations of anionic solvation,[8] since coördination through the ammonium ion is improbable. Ammonation of ammonium salts, especially at lower temperatures, occurs far more frequently than hydration. Unless this ammonation can be attributed to a coördination of simple or associated ammonia molecules through the ammonium ion, it seems inevitable that it must be ascribed to solvation of the anion.

In the system ammonium trinitride–ammonia the diammonate is believed to exhibit anionic solvation. Whether coördination takes place through hydrogen or through nitrogen atoms, however, is a question to which the final answer cannot as yet be given. The pentammonate, on the other hand, with its inversion temperature at −71°, probably does not show exclusively anionic ammonation, but may rather be identical with the diammonate, except that each of the three ammonia molecules has undergone dimerization.[9] This is equivalent to an assumption that one molecule of ammonia is coördinated with the ammonium ion, and that four molecules, or two diammonol molecules, with the trinitride ion. The formula of the pentammonate may on this basis be written $[NH_3 \cdot NH_4]^+ [N_3 \cdot 2(NH_3)_2]^-$.

Summary

Pressure–temperature–concentration relationships of the system ammonium trinitride–ammonia have been investigated over ranges from 0 to 4000 mm., −90 to +30°, and 0 to 100% ammonia. Two solvates, *ammonium trinitride diammonate*, $NH_4N_3 \cdot 2NH_3$, and *ammonium trinitride pentammonate*, $NH_4N_3 \cdot 5NH_3$, both of which are white crystalline solids, have been obtained. The diammonate undergoes inversion into anammonous salt at −9°; the pentammonate undergoes inversion into the diammonate at −71°. The eutectic is located at −87° and 76% ammonia.

ITHACA, N. Y. RECEIVED AUGUST 13, 1934

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[8] Sidgwick, "The Electronic Theory of Valency," Oxford University Press, 1929, p. 194.

[9] In all probability liquid ammonia, like water, is associated, and contains such molecular species as NH_3, *ammonol*, $(NH_3)_2$, *diammonol*, and $(NH_3)_3$, *triammonol*, analogous to hydrol, dihydrol and trihydrol.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Activity Coefficients of Sulfuric Acid at Temperatures from 0 to 50°[1]

BY JOSEPH SHRAWDER, JR., AND IRVING A. COWPERTHWAITE

Galvanic cells involving sulfuric acid have been studied by a number of investigators.[2] With few exceptions the investigations have been confined to the use of the mercury–mercurous sulfate electrode. While this electrode is reversible to sulfate ion and functions nicely in relatively concentrated solutions, the solubility of mercurous sulfate is such[3] as to prohibit its use in solutions more dilute than approximately 0.005 molal. For the evaluation of E^0 it is desirable that measurements be obtained to a lower concentration.

The cell

$$\text{Pb–Hg (2 phase), } PbSO_4(s),\ H_2SO_4(m),\ H_2$$

is well designed to provide the required measurements in the dilute range. The solubility of lead sulfate, 43.5 mg. per liter in pure water at 20°,[4] is sufficiently low in dilute acid to obviate any large correction from this source.

Previous attempts to measure the potential of the above cell have been made by Lewis and Brighton,[5] Vosburgh and Craig,[6] and Baumstark.[2e] Of these, only Baumstark was able to secure reproducible results, the other workers reporting deviations of the order of 0.01 volt.

In the present work the electromotive force of this cell has been measured from 0 to 50° over the concentration range 0.02 to 0.001 *m*.

The methods which have been commonly employed for the extrapolation of electromotive force data to infinite dilution vary from simple graphical extrapolations, on the one hand, through a variety

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[1] This paper is from a dissertation presented by Joseph Shrawder, Jr., to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] (a) Brönsted, *Z. physik. Chem.*, **68**, 693 (1909); (b) Edgar, Thesis, Massachusetts Institute of Technology, 1912; (c) Lewis and Lacy, THIS JOURNAL, **36**, 804 (1914); (d) Randall and Cushman, *ibid.*, **40**, 393 (1918); (e) Baumstark, Dissertation, Catholic University of America, 1932.

[3] Harned and Sturgis, THIS JOURNAL, **47**, 945 (1925).

[4] Purdum and Rutherford, *ibid.*, **55**, 3221 (1983).

[5] Lewis and Brighton, *ibid.*, **39**, 1906 (1917).

[6] Vosburgh and Craig, *ibid.*, **51**, 2009 (1929).

of empirical methods, to the functional methods based on the Debye–Hückel theory. The complete solution of the Debye–Hückel equation through the third approximation for the case of unsymmetrical valence type electrolytes has been made available by means of tables communicated by La Mer, Gronwall and Greiff.[7] However, the validity of extensions of the Debye–Hückel theory to the cases of unsymmetrical valence type electrolytes and of electrolytes giving ions of unequal size has been brought into question by Halpern.[8] In addition, the incomplete dissociation of the bisulfate ion contributes to the uncertainty involved in any application of the Debye–Hückel theory to sulfuric acid solutions.

The work of Hamer[9] in measuring the dissociation constant of the bisulfate ion over a wide range of temperatures has offered the possibility of applying this parameter in an effort to obtain E^0 without recourse to postulates other than the limiting law of Debye. This is desirable since the conclusions of Halpern confirm the functional nature of the limiting law (*i. e.*, the square root dependence, if not the constant).

Experimental Methods

Since the electrodes employed require oxygen-free conditions, a cell similar to that employed by Cowperthwaite, La Mer and Barksdale[10] has been used. With the exception of a hydrogen inlet tube added to the base of the central compartment, the cell employed here differs only in dimensions from that used by the above authors. The technique employed with this type of cell has been presented elsewhere.[10]

One unique feature of the manipulation consists in the use of dried lead sulfate in the lead amalgam–lead sulfate electrode. Previous workers[11] have followed the procedure of storing the lead sulfate under water. In the present work the lead sulfate was dried, powdered and added to the amalgam limbs immediately after the amalgam was introduced. The addition of sufficient solid lead sulfate to leave a thin film over the surface of the amalgam has given excellent results. Electrodes prepared in this manner checked among themselves to better than 0.1 mv.

The hydrogen electrodes employed were of two types. For the higher concentrations the standard black electrodes were found to be satisfactory. For the concentration 0.002 *m* and below, better results were obtained using bright platinum electrodes. These were prepared following the directions given by Lorch.[12] Four hydrogen electrodes were used in each cell, the average deviation being of the order of 0.02 mv. The hydrogen electrodes were freshly plated for each cell.

Apparatus.—The type K potentiometer, Eppley standard cell, and thermometers were calibrated and frequently checked during the course of the investigation. Water thermostats were used with temperature control maintained to ±0.02°.

Lead Nitrate.—Baker Analyzed salt was recrystallized four times, filtered by suction and dried at 110°.

Sulfuric Acid.—C. P. sulfuric acid was redistilled three times in a Pyrex still at atmospheric pressure. The final distillate was then diluted with sufficient distilled water to make nine liters of approximately half molar solution. This stock solution, from which all the solutions subsequently studied were made by weight dilution, was stored in a large Pyrex bottle and was carefully analyzed at intervals of two months by precipitation as barium sulfate, and by titration against acid potassium phthalate using carbonate-free sodium hydroxide solution as an intermediate. Weight burets were employed in this titration. The concentration of the stock solution was known to one part in four thousand.

Lead Sulfate.—This was prepared by adding a 0.5 molar solution of sulfuric acid to a 10% solution of purified lead nitrate. The product was washed by decantation for two weeks, after which it was filtered and dried at 110°.

Mercury and **hydrogen** were purified in accordance with standard procedure.

Lead Amalgam.—The amalgams were prepared electrolytically following the directions of La Mer and Parks,[11a] and were stored in reservoirs of the type described by Cowperthwaite and La Mer.[11b] Attempts to obtain satisfactory amalgams from stick lead and purified mercury were uniformly unsuccessful, due to the difficulty encountered in obtaining lead of sufficient purity.

Theoretical

The cell upon which measurements have been made may be represented as

$$\text{Pb-Hg (2 phase)}, \ PbSO_4(s), \ H_2SO_4(m), \ H_2 \qquad (1)$$

for which the corresponding cell reaction is

$$\text{Pb (2 phase amalgam)} + H_2SO_4(m) = PbSO_4(s) + H_2 \qquad (2)$$

The conventions employed here and in what follows are those established by Lewis and Randall, whose nomenclature will be followed throughout.

With the reactions written in the direction indicated, the cell potential is positive in sign, and the substance of variable activity occurs to the left of the equality sign. The equation for the cell potential becomes, therefore

$$E = E^0 + \frac{3RT}{nF} \ln 4^{1/3} m + \frac{3RT}{nF} \ln f \qquad (3)$$

as may be verified by reference to the free energy equation and the definition of $m^{\pm}$. The function $E^{0\prime}$ may then be defined as

$$E^{0\prime} = E - \frac{3RT}{nF} \ln 4^{1/3} m \qquad (4)$$

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

[8] Halpern, *J. Chem. Phys.*, **2**, 85 (1934).

[9] Hamer, THIS JOURNAL, **56**, 860 (1934).

[10] Cowperthwaite, La Mer and Barksdale, *ibid.*, **56**, 544 (1934).

[11] (a) La Mer and Parks, *ibid.*, **53**, 2040 (1931); (b) Cowperthwaite and La Mer, *ibid.*, **53**, 4333 (1931); (c) Bray, *ibid.*, **49**, 2372 (1927).

[12] Lorch, Dissertation, Columbia University, 1932.

so that

$$E^0 = E^{0\prime} - \frac{3RT}{nF} \ln f \qquad (5)$$

In the equations used thus far, no recognition has been given the fact of incomplete dissociation of the bisulfate ion. If, instead of the total acid concentration, the stoichiometric concentration of ions is employed in equation (4), a new function is thereby defined. This will be denoted by the symbol E^{0*}.

The quantity E^{0*} for an incompletely dissociated electrolyte is thus the analog of the quantity $E^{0\prime}$ for the completely ionized electrolytes. For the case of sulfuric acid, it can be shown that

$$\begin{aligned} m_{\pm} &= \sqrt[3]{m^2(1+\alpha)^2 m\alpha} \\ &= m(1+\alpha)^{2/3}\,\alpha^{1/3} \end{aligned} \qquad (6)$$

and

$$\begin{aligned} E^{0*} &= E - \frac{3RT}{nF} \ln m\,(1+\alpha)^{2/3}\,\alpha^{1/3} \\ &= E - \frac{3RT}{nF} \ln m\,\alpha^{1/3} - \frac{3RT}{nF} \ln (1+\alpha)^{2/3} \end{aligned} \qquad (7)$$

Also

$$E^0 = E^{0*} - \frac{3RT}{nF} \ln f \qquad (8)$$

Equations (5) and (8) may be used to compute activity coefficients for sulfuric acid at each of the temperatures and concentrations studied. The activity coefficients presented in this paper have been computed on the basis of equation (5). These have been called by Brönsted[13] "stoichiometrical activity coefficients."

Experimental Data and Calculations

The correction for the solubility of lead sulfate in the calculation of $E^{0\prime}$ and E^{0*} was made by separating the ln m terms in equations (4) and (7) into two parts, one for the sulfate ion and one for the hydrogen-ion concentration. Then equations (4) and (7) become, respectively

$$E^{0\prime} = E + \frac{2RT}{nF} \ln m_1 + \frac{RT}{nF} \ln m_2 + \frac{RT}{nF} \ln 4 \qquad (9)$$

$$\begin{aligned} E^{0*} = E &+ \frac{2RT}{nF} \ln m_1\alpha^{1/3} + \\ &\frac{RT}{nF} \ln m_2\alpha^{1/3} + \frac{3RT}{nF} \ln (1+\alpha)^{2/3} \end{aligned} \qquad (10)$$

where m_I is the gross molality of the acid and $m_2 = m_1 +$ the molal solubility of lead sulfate in sulfuric acid of molality m. The solubility of lead sulfate in the various dilute solutions of sulfuric acid has been calculated from the measurements of Purdum and Rutherford[4] at 20°, Pleissner[14] at 18° and Huybrechts and Ramelot[15] at 18 and 30°. The measurements of these workers extend over the entire range of acid concentrations studied in this work. The desired solubility data were obtained by plotting the available data on a large scale followed by interpolation to the required concentrations and extrapolation to the required temperatures.

Table I records the calculated solubilities in millimoles per liter in sulfuric acid of the indicated molalities.

TABLE I

CALCULATED SOLUBILITY OF LEAD SULFATE IN SULFURIC ACID OF MOLALITY m (MILLIMOLES PER LITER)

m	0°	12.5°	25°	37.5°	50°
0.02	0.0099	0.0124	0.0152	0.0183	0.0220
.01	.0107	.0134	.0166	.0199	.0238
.005	.0122	.0153	.0189	.0227	.0273
.002	.0170	.0213	.0262	.0314	.0377
.001	.0238	.0299	.0372	.0448	.0541

Calculation of α

In the calculation of E^{0*}, values for α, the degree of ionization of bisulfate ion, are required. The data given by Hamer[9] along with the calculated solubilities of lead sulfate may be employed in this computation. The expression for the second dissociation constant of sulfuric acid is

$$\frac{f_{H^+}\, m_{H^+}\, f_{SO_4^=}\, m_{SO_4^=}}{f_{HSO_4^-}\, m_{HSO_4^-}} = K_2 \qquad (11)$$

We may assume that the activity coefficients of the hydrogen and bisulfate ions will cancel, since they are activity coefficients of univalent ions in a solution of low ionic strength. Then if the concentration of bisulfate ion is denoted by x, the expression becomes

$$\frac{(2m_1 - x)\,(m_2 - x)}{(x)} = \frac{K_2}{f_{SO_4^=}} \qquad (12)$$

where m_1 and m_2 have the significance previously indicated. The activity coefficient of the sulfate ion has been assumed to be equal to $f_{\pm}$ for a typical bi-bivalent sulfate and has been computed by use of the extended theory of Gronwall, La Mer and Sandved employing an ion size of 3.64 Å. The choice of this value for "a" was prompted by the agreement obtained by La Mer and Parks[11a] and Cowperthwaite and La Mer [11b] using this ion size in applying the extended theory to cadmium sulfate and zinc sulfate, respectively. Since equation (12) contains the two mutually dependent unknowns $f_{SO_4^=}$ and x, it has been necessary to employ a series of approximations in its solution. From the calculated values of x, the corresponding values of α may be obtained

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[13] Brönsted, THIS JOURNAL, **42**, 761 (1920).

[14] Pleissner, *Arb. Kaiser, Ges. Amt.*, **26**, 419 (1907).

[15] Huybrechts and Ramelot, *Bull. soc. chim. Belg.*, **36**, 239 (1927).

directly. Table II gives the values for α, thus calculated, along with the dissociation constants from which they are derived.

TABLE II

THE DEGREE OF IONIZATION OF HSO_4^-

m	0°	12.5°	25°	37.5°	50°
			K_2		
	0.0148	0.0137	0.0120	0.0102	0.00794
			α		
0.02	0.5509	0.5375	0.5090	0.4799	0.4174
.01	.6620	.6487	.6245	.5944	.5353
.005	.7586	.7470	.7257	.6993	.6469
.002	.8597	.8512	.8355	.8152	.7768
.001	.9124	.9062	.8949	.8799	.8515

$E^{0\prime}$ and E^{0*} may now be calculated on the basis of equations (9) and (10). Table III gives the observed values of the electromotive force corrected to one atmosphere partial pressure of hydrogen, along with the corresponding values of $E^{0\prime}$ and E^{0*}.

TABLE III

VALUES OF E(OBS.), $E^{0\prime}$ AND E^{0*}

m		0°	12.5°	25°	37.5°	50°
	E(obs.)	0.09536	0.09555	0.09589	0.09625	0.09651
0.001	$E^{0\prime}$	.32251	.33302	.34366	.35432	.36483
	E^{0*}	.32463	.33541	.34648	.35768	.36922
	E(obs.)	.11725	.11799	.11895	.11985	.12050
.002	$E^{0\prime}$	.32012	.33012	.34032	.35048	.36036
	E^{0*}	.32361	.33400	.34484	.35581	.36717
	E(obs.)	.14487	.14622	.14745	.14890	.15037
.005	$E^{0\prime}$	.31549	.32463	.33366	.34291	.35217
	E^{0*}	.32175	.33154	.34156	.35205	.36365
	E(obs.)	.16443	.16588	.16744	.16909	.17067
.01	$E^{0\prime}$	.31060	.31873	.32698	.33532	.34358
	E^{0*}	.31981	.32881	.33836	.34834	.35963
	E(obs.)	.18301	.18467	.18637	.18828	.19004
.02	$E^{0\prime}$	.30473	.31196	.31922	.32671	.33404
	E^{0*}	.31772	.32606	.33513	.34458	.35577

The Extrapolation for E^0

In Fig. 1, $E^{0\prime}$ has been plotted against $m^{1/2}$ while Fig. 2 gives the function E^{0*} plotted in a similar manner. The Debye limiting slopes for the various temperatures have been included on both plots. It will be observed that the function E^{0*} approaches the limiting slope as the concentration is decreased. E^0 has been evaluated at each temperature by taking the values of E^{0*} which fall on the limiting slope and adding to them appropriate values of $3RT/nF \ln f$ computed with the aid of the limiting law. The mean of the several values for E^0 thus obtained has been taken as the E^0 for that temperature. Values for E^0 at five temperatures are given in Table IV.

TABLE IV

t, °C.	0	12.5	25.0	37.5	50.0
E^0	0.32810	0.33919	0.35052	0.36192	0.37376

The activity coefficients given in Table V have been obtained by the introduction of the appropriate values for E^0 and $E^{0\prime}$ into equation (5).

TABLE V

STOICHIOMETRIC ACTIVITY COEFFICIENTS OF SULFURIC ACID

m	0°	12.5°	25°	37.5°	50°
0.02	0.516	0.478	0.444	0.416	0.386
.01	.609	.574	.543	.515	.485
.005	.700	.674	.646	.623	.596
.002	.798	.782	.767	.752	.725
.001	.853	.846	.837	.828	.807

Discussion of Results

Despite any theoretical objections to the use of the La Mer, Gronwall and Greiff extension of the Debye-Hückel theory, it is of interest to inquire as to whether or not the extended theory will fit the data and be of service as a method of extrapolation. We have therefore carried out the calculations necessary to compare the theory with the experimental data at 25°. In this computation an ion size of 1.75 Å. has been employed. The results are indicated graphically on Fig. 3 with circles denoting experimental points and the solid line A representing the extended theory. Crosses have been added to represent the values for $E^{0\prime}$ obtained by Baumstark[2e] at 25°. The value for

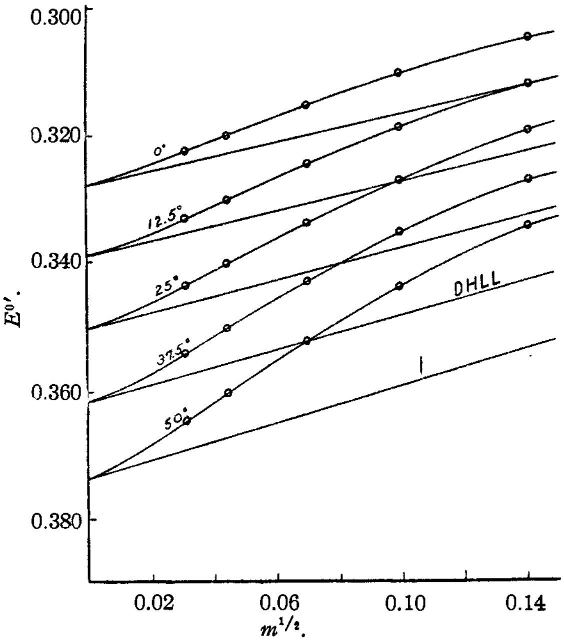

Fig. 1.

E^0 used is that obtained using the extrapolation of the function E^{0*} as previously explained, so that the curve drawn represents the best approach to the experimental data obtainable by adjustment of the ion size parameter. While the agreement is unsatisfactory, it should be pointed out that the theory does not provide convergent values for ln f when only three terms are employed in the case of such a small ion size. In its present form, the third term of the series is of the same order of magnitude as the first.

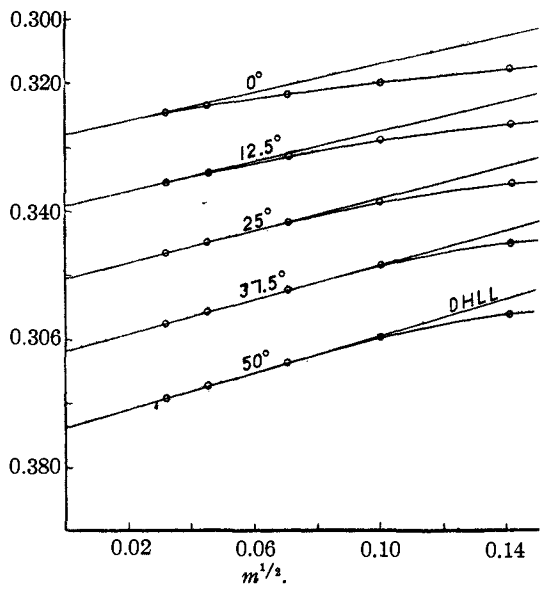

Fig. 2.

In addition to the experiment points for $E^{0\prime}$ and the extended theory curve, A, Fig. 3 also contains the limiting slope, B, and the experimental points corresponding to the function E^{0*}. Through the latter points has been passed a smooth curve, C, which fuses with the limiting slope. While the point of fusion appears to vary somewhat with temperature (Fig. 2), still the adherence is such as to warrant the use of the limiting law in the extrapolation for E^0. While the function $E^{0\prime}$ must also extrapolate to E^0, the extrapolation is complicated by the nature of the curve. If the $E^{0\prime}$ function is to fuse with the limiting law, at low concentrations, it must exhibit a reversal of curvature at some point. The complete solution of the Debye–Hückel theory predicts just such a form of curvature in very dilute solution, but, as pointed out, it is not possible to obtain a quantitative evaluation of the theory in the case of sulfuric acid. It has seemed expedient therefore to use the function E^{0*} and rely upon the limiting law. The values for E^0 thus obtained are probably accurate to 0.1 millivolt. The value for E^0 at 25° differs from that obtained by Baumstark by 1.65 millivolts, which difference may be assigned to the difference in methods of extrapolation since Baumstark extrapolated the $E^{0\prime}$ curve linearly.

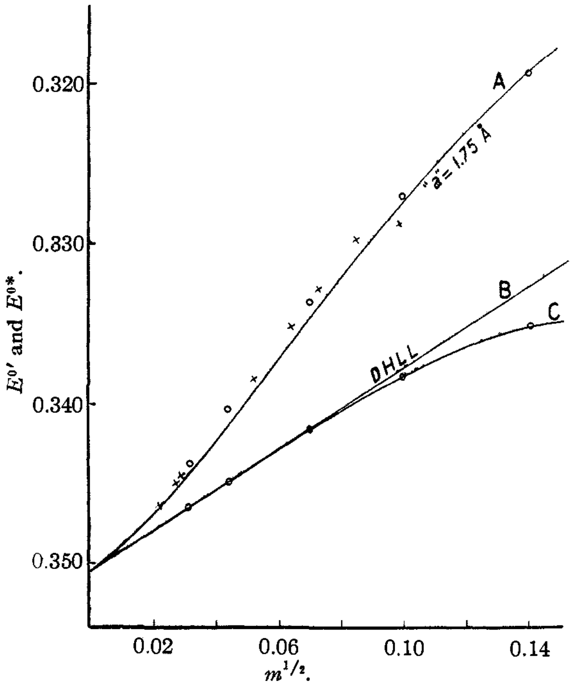

Fig. 3.—At 25°.

It is of interest to compare the activity coefficients obtained in this work with those obtained by other methods. Table VI lists the coefficients calculated from equation (5) (column 1) with those given by Lewis and Randall, Randall and Scott[16] from the freezing point measurements, and Baumstark.[2e]

TABLE VI

STOICHIOMETRICAL ACTIVITY COEFFICIENTS OF SULFURIC ACID

m	I	II Baumstark	III L. & R.	IV R. & S.
0.02	0.444		0.519	0.553
.01	.543		.617	.648
.005	.646	0.615	.696	.734
.002	.767	.735	.782	.825
.001	.837	.804	.831	.876

The values obtained for the activity coefficients are smaller than those given by Randall and Scott and are larger than those of Baumstark. The latter difference arises from the difference in E^0 values used. The values obtained by the freezing

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[16] Randall and Scott, THIS JOURNAL, **49**, 647 (1927).

point method are subject to difficulties associated with extrapolation which are fully as severe as with the electromotive force method, and are particularly aggravated in this case of an incompletely dissociated unsymmetrical valence type electrolyte.

Summary

1. The electromotive force of the cell Pb-Hg (2 phase), $PbSO_4(s)$, $H_2SO_4(m)$, H_2 has been measured for the concentrations 0.02, 0.01, 0.005, 0.002 and 0.001 m at each of the temperatures, 0, 12.5, 25, 37.5 and 50°.

2. A new method has been devised for extrapolating to infinite dilution, taking into account the incomplete dissociation of the bisulfate ion, by means of which E^0 has been obtained for each temperature.

3. The activity coefficient of sulfuric acid has been evaluated at each temperature for the five concentrations studied.

NEW YORK CITY RECEIVED AUGUST 15, 1934

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Partial Molal Heat of Dilution of Sulfuric Acid from Electromotive Force Measurements[1]

BY IRVING A. COWPERTHWAITE AND JOSEPH SHRAWDER, JR.

In a previous paper,[2] electromotive force measurements at concentrations from 0.001–0.02 m and extrapolated values for E^0 were given for the cell

$$\text{Pb-Hg, PbSO}_4\text{(s), H}_2\text{SO}_4(m)\text{, H}_2 \qquad (1)$$

at 12.5° intervals from 0–50°. The reaction for this cell is

$$\text{Pb (satd. with Hg)} + \text{H}_2\text{SO}_4(m) \longrightarrow \text{PbSO}_4\text{(s)} + \text{H}_2 \text{ (1 atm.)} \qquad (2)$$

As the sulfuric acid is the only reactant of variable activity, these data used in connection with the Gibbs–Helmholtz equation permit the computation of the partial molal heat of dilution of sulfuric acid. It has been shown by La Mer and associates,[3] that the introduction of the function $E^{0\prime} = E - (\nu RT/nF) \ln m$ into the Gibbs–Helmholtz equation gives the convenient form

$$-\Delta H = nF\left(E^{0\prime} - T\frac{dE^{0\prime}}{dT}\right) \qquad (3)$$

This form of the equation is particularly useful in that it may be used in the evaluation of $-\Delta H^0$ since $E^{0\prime}$ extrapolates smoothly to E^0 at infinite dilution.

In order to obtain the temperature coefficients required in the above equation, an analytical function has been set up for each of the concentrations studied, in which $E^{0\prime}$ is expressed in the following manner

$$E^{0\prime} = A + Bt + Ct^2 + Dt^3 \qquad (4)$$

The constants for these equations have been determined by the method of least squares. This method was selected in order to obtain a smoothing of the experimental data with a view to securing reliable derivatives. Equations of the quadratic type have been found to fit the experimental points almost as well as the cubic type used; however, the improvement secured by use of the cubic equations appeared to be sufficient to warrant the use of the four constant equations. The values for the constants of equation (4) for the various concentrations are given in Table I.

TABLE I

CONSTANTS FOR THE EQUATION: $E^{0\prime} = A + Bt + Ct^2 + Dt^3$

m	A	$B \times 10^4$	$C \times 10^7$	$D \times 10^9$
0.000	0.32810	8.8717	1.029	8.294
.001	.32251	8.3111	9.015	−11.905
.002	.32012	7.8564	14.059	−20.454
.005	.31549	7.2306	2.068	0.116
.01	.31060	6.4117	7.918	− 8.447
,02	.30473	5.6728	7.683	− 7.729

By use of the above coefficients, the first derivative of $E^{0\prime}$ with respect to the temperature has been evaluated at 25° for each of the values for m. The calculation of $-\Delta H$ and of $\bar{L}_2$ is then readily carried out. The important quantities used in the thermal calculations have been summarized in Table II.

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(1) This paper is from a dissertation submitted by Joseph Shrawder, Jr., to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Shrawder and Cowperthwaite, THIS JOURNAL. **56**, 2340 (1934).

(3) La Mer and Parks, *ibid.*, **53**, 2040 (1931); La Mer and Cowperthwaite, *ibid.*, **55**, 1004 (1933); Cowperthwaite, La Mer and Barksdale, *ibid.*, **56**, **544** (1934).