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.

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[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).

TABLE II

THE COMPUTATION OF $-\Delta H$ AND $\bar{L}_2$

m	$E^{0\prime}$	$dE^{0\prime}/dT$	$-\Delta H$	$\bar{L}_2$
0.000	0.35052	0.00090785	3687	0
.001	.34366	.00085386	4113	426
.002	.34032	.00081759	4458	771
.005	.33366	.00073362	5305	1618
.01	.32698	.00066492	5942	2255
.02	.31922	.00059121	6598	2911

The values of $\bar{L}_2$ recorded in Table II have been plotted against $m^{1/2}$ in Fig. 1. Values of $\bar{L}_2$ obtained calorimetrically by Lange, Monheim and Robinson[4] are given on the same graph. The two methods will be seen to yield widely divergent results for $\bar{L}_2$. In particular, the methods fail to agree as to the form of the $\bar{L}_2$ curve at very low concentrations. The calorimetric data, when plotted against $m^{1/2}$, provide a curve which becomes linear below approximately 0.001 m. In the same region, the data which we have obtained indicate not a linear function, but one which exhibits a point of inflection such as would be required to bring the curve into the limiting slope of Debye and Hückel. This limiting slope has been indicated on Fig. 1 and has been calculated from the equation given by La Mer and Cowperthwaite.[3] For a 1–2 electrolyte, it may be shown that the limiting law becomes $\bar{L}_2 = 3041\ m^{1/2}$.

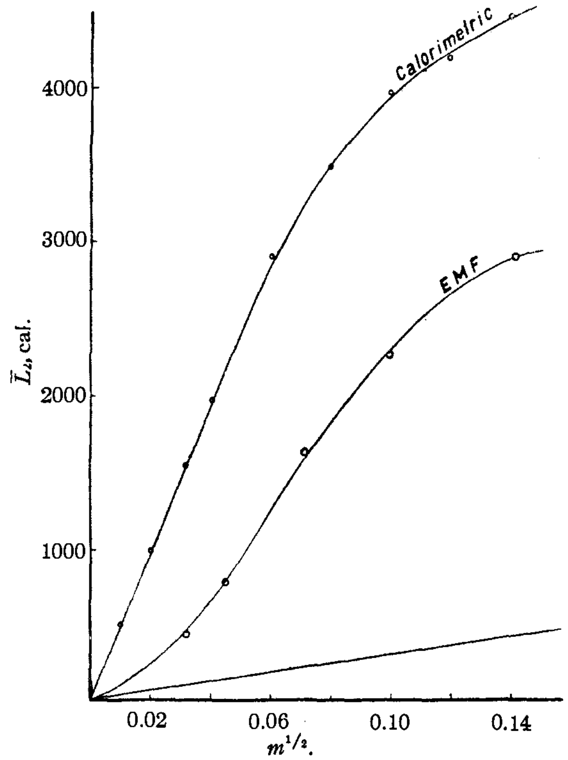

Fig. 1.—At 25°.

That the difference in method of extrapolation is responsible for a large part of the differences between our $\bar{L}_2$ values and those given by Lange, Monheim and Robinson, will be evident from the following considerations. The excess partial molal heat content of sulfuric acid relative to some arbitrary initial concentration, other than $m = 0$, can be computed from the data obtained by the two methods. If a reference concentration above the controversial region of extrapolation is selected, we may demonstrate whether or not the two methods yield similar increments of partial molal heat content at higher concentrations. This has been done using $m = 0.0036$ ($m^{1/2} = 0.06$) as a convenient reference state, and values thus obtained have been plotted against $m^{1/2}$ in Fig. 2. It will be observed that, using this procedure, the relative partial molal heat content ($\overline{He}$) becomes zero at $m = 0.0036$ and that adequate agreement above this concentration is obtained between the two methods. In Fig. 2, our values are given by the solid line, while the circles indicate the data of Lange, Monheim and Robinson. The choice of reference state has been prompted by the agreement above this concentration and the increasing divergence of the data below.

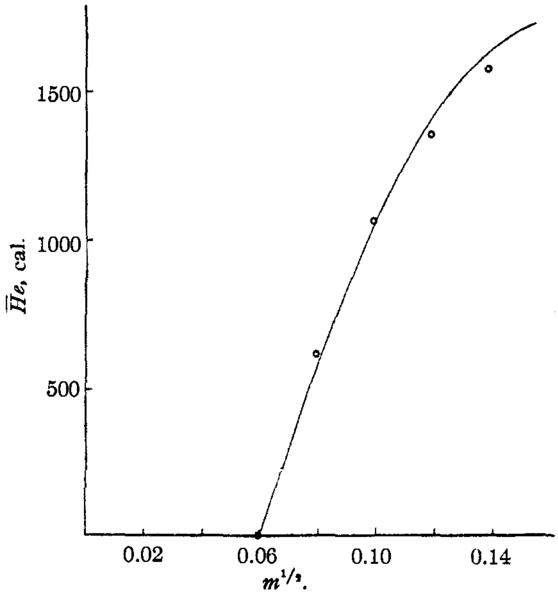

Fig. 2.—At 25°.

It is to be pointed out that the calorimetric data for $\bar{L}_2$ have been obtained by a linear extra-

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[4] Lange, Monheim and Robinson, THIS JOURNAL, **55, 4733** (1933).

polation of the integral heats of dilution obtained from direct measurement. The value for $-\Delta H^0$, on the basis of which the $\bar{L}_2$ values are calculated in the electromotive force method, depends upon the extrapolated values for E^0. However, it should be observed that the value for E^0 is subject to confirmation by comparison with data obtained by other investigators on other electrolytes. For example, we can obtain a value for E^0-(H_2SO_4) of the cell Pb-Hg, $PbSO_4$(s), H_2SO_4(*m*) H_2 by combining the E^0 ($ZnSO_4$) for the cell Zn-, Hg, $ZnSO_4$(*m*), $PbSO_4$(s), Pb-Hg determined by Cowperthwaite and La Mer,[5] with the E^0-(HCl) for the cell H_2, HCl(*m*), AgCl(s), Ag(s) measured by Carmody,[6] and the E^0($ZnCl_2$) for the cell Zn-Hg, $ZnZl_2$(*m*), AgCl(s), Ag(s) found by Scatchard and Tefft.[7] If we use the values E^0 ($ZnSO_4$) = 0.4109, E^0(HCl) = 0.2222, and E^0-($ZnCl_2$) = 0.9834, we obtain a value E^0(H_2SO_4) = 0.3503. If, on the other hand, we use the E^0-($ZnCl_2$) = 0.9837 extrapolated by La Mer, Gronwall and Greiff,[8] using the data of Scatchard and Tefft, we find E^0(H_2SO_4) = 0.3506. These values are in excellent agreement with the value of E^0(H_2SO_4) = 0.3505 found by the authors.[2] If, for purposes of comparison, the E^0 necessary to provide the $-\Delta H^0$ required by the calorimetric data is calculated (assuming our computed temperature coefficient to be correct), it will be found that the value is E^0 = 0.3135. It is difficult to see how even the most crude method of extrapolation could yield a value of this magnitude. It is also noteworthy that the present values of $\bar{L}_2$ have been secured without the use of any theoretical extensions of the Debye–Hückel theory and that the "hump" in the curve is still obtained. This eliminates the extended theory as the cause of the inflection.

Each value of $-\Delta H$ is computed on the basis of five values of $E^{0\prime}$ measured through a temperature interval of fifty degrees. If we assume the precision of these values to be ±0.00005 volt, the maximum error in $dE^{0\prime}/dT$ would be ±0.000002 volt per degree, corresponding to a maximum uncertainty of ±30 calories in $-\Delta H$. It may also be shown that, if the temperature coefficients are accepted as valid, the error introduced into the values of $-\Delta H$ by an error of 0.0001 volt in E will be only 5 calories. In consequence, of these considerations, it would seem that the observed hump in the $\bar{L}_2$ curve is too large to be attributed to experimental error and that the data indicate a distinct tendency on the part of the curve to approach the Debye–Hückel limiting slope for this function.

At present, it appears that there is a real discrepancy between values of the partial molal heat of dilution of electrolytes in dilute solution determined from electromotive force measurements and those obtained from calorimetric experiments. This is a conclusion which requires further investigation.

Summary

The partial molal heat of dilution of sulfuric acid has been computed by means of the Gibbs–Helmholtz equation using electromotive force data for the cell Pb-Hg, $PbSO_4$(s), H_2SO_4 (*m*), H_2.

Evidence has been presented to show that the hump type of curve obtained when the partial molal heat of dilution is plotted against the square root of the concentration is independent of any extension of the Debye–Hückel theory, and is experimentally valid. This is contrary to the results of calorimetric work where linear proportionality against the square root of concentration is reported.

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[5] Cowperthwaite and La Mer, THIS JOURNAL, **53**, 4333 (1931).

[6] Carmody, *ibid.*, **54**, 188 (1932).

[7] Scatchard and Tefft, *ibid.*, **52**, 2272 (1930).

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