[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF INDIANA UNIVERSITY]

The Standard Electrode Potentials of the Mercury–Mercurous Sulfate Electrode in Methanol at 20, 25, 30 and 35°[1]

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Electromotive force studies have been reported for solutions of sulfuric acid in methanol,[4] and in ethanol,[5] using hydrogen and mercury–mercurous sulfate electrodes in cells without liquid junctions. In neither instance was it possible to determine the standard electrode potentials by direct extrapolation methods. Rather, such values were calculated by applying the extended Debye–Hückel equation to data in relatively concentrated solutions. This method of approximation was based on the seemingly reasonable assumption that both the primary and secondary ionization steps of the dibasic sulfuric acid are virtually complete in dilute solutions.

However, recent electrolytic conductivity studies[6,7] have demonstrated that the complete dissociation hypothesis is erroneous and, even in dilute solutions in methanol, sulfuric acid can be described essentially as an incompletely dissociated univalent electrolyte. In the course of these same conductivity measurements it was noted that a slow reaction seemed to occur between the sulfuric acid and the methanol and special precuations were necessary to prevent this effect from obscuring the results of the investigation. Because these effects were not obvious in the earlier electromotive force study of the sulfuric acid–methanol system,[4] the previously published data may be somewhat in error. Since it was believed that the conductivity investigations disclosed techniques that could effect notable refinement of accuracy for electromotive force methods, it was thought desirable to repeat in part the earlier investigations[4] and also to extend the use of the improved methods to make a more extensive thermodynamic study of the same system. Consequently, it was the objective of this investigation to determine the standard electrode potentials of the mercury–mercurous sulfate electrode in a manner independent of the Debye–Hückel equation, and thereby make it possible to compute stoichiometric activity coefficients. Such data, derived from an independent thermodynamic method, can be used to check the consistency and validity of the conclusions deduced for the same system from the conductivity data[6,7] which were interpreted on the basis of the fundamental assumption of the validity of the Debye–Hückel equation.

Measurements were made at 20, 25, 30 and 35° on the cell

$$(Pt)H_2\text{–}H_2SO_4 \text{ in methanol–}Hg_2SO_4, Hg$$

In addition to the primary objective already described, it is obvious that these data make possible the calculation of the temperature coefficients of the electromotive force and, thereby, through the application of the Gibbs–Helmholz equation, approximations can be made of the partial molal heats of dilution. However, such calculations of the partial molal heats of dilution are very sensitive to small experimental errors, and it is the conviction of the authors that even the more advanced techniques of measurement in non-aqueous solutions are as yet of insufficient precision and accuracy to provide an adequate evaluation of thermochemical constants for any finely discriminate theoretical purposes. Hence, this implication of the data, although indicated, should not be construed as a primary objective of this investigation.

Procedure

The procedures for the purification and drying of methanol have been described in previous papers from this laboratory.[6,8] The pure sulfuric acid, as prepared by the method of Kanning, Bobalek and Byrne,[6] had a melting point of 10.47 ± 0.03°, which remained constant for a period of several weeks if the acid was stored in glass-stoppered flasks set in a phosphorus pentoxide desiccator.

Mercurous sulfate was purified by dissolving the C. P. grade of reagent in concentrated sulfuric acid in the presence of triple-distilled mercury, and then reprecipitating the salt by adding the acid solution dropwise to a large excess of anhydrous methanol. The mixture of the precipitate and mercury was washed about twenty times by decantation with anhydrous methanol. The clear white color of the final product seemed to indicate that this technique induced no hydrolysis of the mercurous sulfate.

Commercial, electrolytic hydrogen was purified by flowing the gas through an all-glass train of absorption tubes containing in series concentrated sulfuric acid, solid potassium hydroxide, copper gauze at 550°, potassium hydroxide and "Drierite."

The cell potentials were measured with a Leeds and Northrup Type K-2 potentiometer and a Type R reflecting galvanometer.

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[1] This paper is constructed from a dissertation presented by Melvin G. Bowman to the Faculty of the Graduate School of Indiana University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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[4] Kanning and Waltz, THIS JOURNAL, **64**, 2676 (1941).

[5] Scholl, Hutchinson and Chandlee, *ibid.*, **57**, 2542 (1925).

[6] Kanning, Bobalek and Byrne, *ibid.*, **65**, 1111 (1943).

[7] Kanning, Byrne and Bobalek, *ibid.*, **66**, 1700 (1944).

[8] Kanning and Campbell, *ibid.*, **64**, 517 (1942).

In the preparation of hydrogen electrodes, a centimeter square of platinum foil was welded at one corner to a platinum wire which was then sealed into soft glass tubing so that the glass covered the weld. The catalytic life of hydrogen electrodes in methanol is relatively short. Several variations were tried in the methods of plating with platinum black in the attempts to prolong the usually short life of the electrode in methanol. The final procedure adopted was the following. (1) Electrolysis as anode in 6 molar hydrochloric acid to clean the platinum. (2) Electrolysis as cathode in 9-molar sulfuric acid to test cleanliness. (Very fine bubbles breaking evenly from the entire surface of the platinum indicate a clean surface.) (3) Electrolysis as cathode in gold cyanide solution (prepared as suggested by Clark[9]) for three minutes at current density of 0.1 ampere. (4) Electrolysis as cathode in chloroplatinic acid solution (prepared as suggested by Hammett and Lorch[10]) for ninety seconds at a current density of 0.3 ampere. The electrode was washed in a stream of distilled water after each electrolysis. After the final washing it was rinsed thoroughly with anhydrous methanol and then soaked for a few minutes in a portion of the cell solution before being transferred to the cell. Special efforts were made to reduce to a minimum the time of exposure to air. The electrodes required approximately fifteen minutes to attain equilibrium. After this time, readings of the cell potentials were constant for thirty to forty-five minutes before the electrodes began to fail. A total catalytic life of approximately one hour in alcohol solutions was noted also by Kanning and Campbell[8] and Nonhebel and Hartley.[11]

The hydrogen was saturated with alcohol from the cell solution by blowing the gas through a sintered-glass disk in a gas-saturator connected in series with the hydrogen-input tube of the cell. The hydrogen was passed upward through a 20-cm. column of the cell solution in the saturator before flowing through a U-tube to the nozzle fitted in the bottom of the cell. The cell was made from the elements of a standard 34/45 ground-glass Pyrex joint. Two-6 mm. tubes were sealed to the bottom of the cell and bent in a U so as to extend parallel to the length of the cell. The junctions of these tubes with the bottom of the cell were prepared so as to permit the formation of two individual electrode pools (1 sq. cm. of surface area) of mercury underneath the layer of mercuric sulfate when mercury was poured to the desired levels in the side tubes. Contact with the potentiometer lead wires was made through the mercury in these side tubes.

The measurements were made with the cell and saturator immersed in an oil-bath that was controlled at the desired temperature with a variation of less than ± 0.01°. Thermometers calibrated by the Bureau of Standards were used in adjusting temperatures.

Methanol was distilled directly into a weighed flask containing mercurous sulfate. Sulfuric acid, in a glass-stoppered vial, was weighed on a microbalance and then the vial was dropped into the weighed quantity of the methanol–mercurous sulfate mixture within the flask. The flask was closed by substituting a wash-bottle arrangement for the glass stopper and, after thorough mixing, the solution was transferred through a ground-glass joint into the cell and saturator by means of hydrogen pressure applied through the wash bottle arrangement. The cap of the cell was fitted with a small ground-glass joint for connection with the solution transfer bottle, and also with a tube for discharging hydrogen into the atmosphere. Hydrogen was passed through the cell and saturator during this transfer and bubbled through the solution during the period of attainment of temperature equilibrium. (The mercurous sulfate electrodes usually achieved equilibrium with the solution within the time required for the cell to come to constant temperature.) The hydrogen electrodes were then introduced by removing the ground-glass joint from the mouth of the cell and substituting a similar cap containing the attached electrode. Measurements were made frequently until the hydrogen electrode lost catalytic activity. For solutions under 0.02 molal, at least two, and sometimes three, hydrogen electrodes were used. The results obtained from various electrode combinations (two mercurous sulfate electrodes and two or three hydrogen electrodes) varied from the mean value by less than ±0.3 millivolt. In more concentrated solutions, particularly at higher temperatures, a slow drift in potential was observed. The drift was usually less than 0.3 millivolt in one-half hour, and approached this value for the more concentrated solutions. This indicated some instability of the more concentrated solutions; hence, the results obtained with the first electrode on the freshly prepared solutions was considered the most representative value at these higher concentrations.

All solutions were prepared immediately following the purification of the alcohol, and measurements made as rapidly as possible after the solutions were prepared.

Data

The measured and corrected cell potentials are listed in Table I.

The correction, ΔE, was computed according to the equation

$$\Delta E = \frac{RT}{2F} \ln \frac{760}{(\text{B.P.} - \text{v.p.})}, \text{ where} \qquad (1)$$

B.P. represents barometric pressure and v.p., the vapor pressure of methanol at the temperature T. The vapor pressure values used are[12] 93.7 mm. at

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(9) Clark, "Determination of Hydrogen Ions," 3rd ed., The Williams and Wilkins Co., Baltimore, Md., 1928, p. 285.

(10) Hammett and Lorch, THIS JOURNAL, **55**, 70 (1933).

(11) Nonhebel and Hartley, *Phil. Mag.*, [6] **50**, 734 (1925).

(12) "International Critical Tables," Vol. III, p. 216.

TABLE I

THE E.M.F. OF THE CELL (Pt)H_2–H_2SO_4 in MeOH–Hg_2SO_4, Hg. at 20°

Molality of H_2SO_4	E(obsd.)	E(cor.)	Molality of H_2SO_4	E(obsd.)	E(cor.)
At 20°			At 25°		
0.0002712	0.7514	0.7533	0.0006999	0.7264	0.7289
.0007632	.7263	.7283	.0011184	.7150	.7174
.0010365	.7187	.7208	.002412	.6971	.6996
.002230	.7005	.7025	.005475	.6780	.6805
.005222	.6813	.6834	.005515	.6772	.6797
.010364	.6657	.6677	.006778	.6731	.6756
.027851	.6458	.6480	.008111	.6687	.6711
.051142	.6357	.6379	.022385	.6484	.6509
.10596	.6240	.6262	.043217	.6363	.6388
.20343	.6119	.6141	.09688	.6224	.6249
.47047	.5988	.6010	.24099	.6073	.6098
			.39613	.6007	.6032
			.46964	.5984	.6009
At 30°			At 35°		
0.0004652	0.7352	0.7387	0.0003649	0.7405	0.7450
.0010385	.7145	.7180	.0009116	.7167	.7212
.0015090	.7062	.7096	.001281	.7096	.7138
.0029620	.6899	.6933	.003091	.6878	.6922
.0051066	.6766	.6801	.004768	.6775	.6818
.010493	.6620	.6653	.011847	.6586	.6630
.024308	.6443	.6478	.022061	.6464	.6508
.062004	.6285	.6321	.052333	.6308	.6352
.10246	.6193	.6229	.11692	.6180	.6224
.20991	.6072	.6109	.18461	.6100	.6144
.45045	.5959	.5995	.41259	.5966	.6010

20°, 122.0 mm. at 25°, 157.4 mm. at 30° and 201.5 mm. at 35°.

Discussion of Results

In the instance where the primary ionization of sulfuric acid is complete and the second ionization negligible, the cell system is described by the equation

$$E = E_0 - \frac{RT}{F}\ln m - \frac{RT}{F}\ln \gamma' \qquad (2)$$

and where the second ionization is complete, by

$$E = E_0 - \frac{3RT}{2F}\ln m - \frac{3RT}{2F}\ln (4^{1/3}\gamma') \qquad (3)$$

where m and γ' represent, respectively, the molal concentration and the stoichiometric activity coefficient. If these equations are differentiated with respect to log m, the last term in each equation becomes negligibly small for very dilute solutions. Accordingly a plot of E *versus* log m for the data at 25° should yield a straight line in the dilute range. The slope of the curve will approach the value −0.05915 if the first ionization is complete and the second negligible, larger negative values if the second ionization step becomes appreciable, and −0.08868 as the secondary ionization step approaches completion. Figure 1 is this plot for the data at 25°. The slope of the curve in the dilute range ($c = -0.056$) indicates that sulfuric acid at these concentrations may be regarded as an incompletely dissociated uni-univalent acid. Similar treatment of data at other temperatures leads to parallel conclusions. This conclusion agrees with the interpretation of the results of earlier measurements of the electrical conductivity of similar solutions.[6,7]

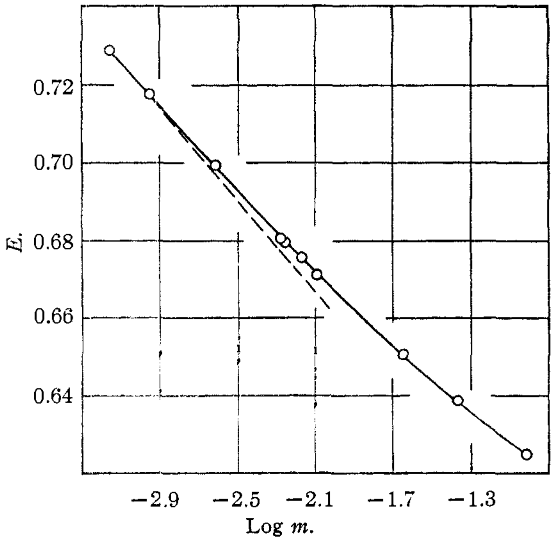

Fig. 1.—Graphical representation of the function used to test the degree of dissociation of sulfuric acid in methanol at 25°. The broken line indicates the maximum slope of the curve (−0.056).

For the purpose of evaluating the standard electrode potential E_0, it is convenient to define the function E', namely

$$E' = E + RT/F\ln m \qquad (4)$$

Assuming that sulfuric acid is fundamentally an univalent electrolyte, as has been established in the preceding discussion, we can define the electromotive force as a function of the activity by the equation

$$E = E_0 - RT/F\ln (m\alpha\gamma_{\pm}) = E_0 - RT/F\ln m - RT/F\ln (\alpha\gamma_{\pm}) \qquad (5)$$

where m and $\gamma_{\pm}$ are, respectively, the molal concentration and molal activity coefficient, and α is the degree of dissociation. The quantity $\alpha\gamma_{\pm}$ can be defined as the stoichiometric activity coefficient γ'; and then, equating (4) and (5), we obtain a function defining E_0 in terms of E' and γ'; namely

$$E' = E_0 - RT/F\ln \gamma' \qquad (6)$$

At high dilutions, α approaches unity, and the difference between the rational activity coefficient, $f_{\pm}$,[13] and molal activity coefficient $\gamma_{\pm}$, becomes negligible; hence

$$-\log \gamma = Ad^{1/2}m^{1/2} \qquad (7)$$

where A is the coefficient of the Debye–Hückel equation and d is the density of pure methanol.

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[13] The conventions and terminology adhered to are those of D. A. MacInnes, "Electrochemistry of Solutions," Reinhold Publishing Corp., New York, N. Y., 1939.

Combining equations (6) and (7), it is established that E' is a function of $m^{1/2}$, and extrapolation to zero concentration will yield the intercept E_0. Graphical methods have established that this function is nearly linear in dilute solutions; thus, confirming the validity of the assumptions made concerning the ionization of the sulfuric acid, and permitting the evaluation of a good approximation of E_0 by extrapolation. The actual extrapolation was effected by fitting to the data a cubic equation of the form

$$E' = E_0 + Am^{1/2} + bm + cm^{3/2} \qquad (8)$$

The constants of this equation, as evaluated by the method of least squares, yielded the following empirical equations

$$E'_{20°} = 0.54428 + 0.0909\ m^{1/2} - 0.0500\ m - 0.0040\ m^{3/2} \qquad (9)$$

$$E'_{25°} = 0.53920 + 0.1079\ m^{1/2} - 0.09956\ m + 0.0467\ m^{3/2} \qquad (10)$$

$$E'_{30°} = 0.53510 + 0.12008\ m^{1/2} - 0.11676\ m + 0.0510\ m^{3/2} \qquad (11)$$

$$E'_{35°} = 0.53177 + 0.13635\ m^{1/2} - 0.12847\ m + 0.0418\ m^{3/2} \qquad (12)$$

The respective E_0 values are 0.5443, 0.5392, 0.5351 and 0.5318. The curve of Fig. 2 describes the data at 25°, and is descriptively representative of the results at other temperatures.

The precision of the determination of E was listed as ±0.3 millivolt. The root-mean-square deviations of the measured value from the values calculated from equations 9 to 12 varied from 0.36 to 0.51 millivolt. Hence, it can be estimated that the cited values of E_0 have been determined to a precision of about ±0.5 millivolt.

Stoichiometric activity coefficients were calculated from the equation (6). E' values were calculated at rounded concentrations from the above cubic equations. Table II lists the γ' values calculated from equation (6) at rounded concentrations.

TABLE II

STOICHIOMETRIC ACTIVITY COEFFICIENTS FOR DILUTE SOLUTIONS OF SULFURIC ACID IN METHANOL

Molality of H_2SO_4	20°	25°	30°	35°
0.0005	0.924	0.912	0.905	0.894
.001	.894	.879	.867	.854
.002	.855	.835	.821	.803
.005	.783	.757	.738	.712
.010	.712	.682	.659	.627
.020	.626	.594	.568	.531
.050	.494	.465	.438	.397
.100	.393	.369	.344	.304
.200	.301	.282	.263	.230
.400	.236	.209	.199	.181

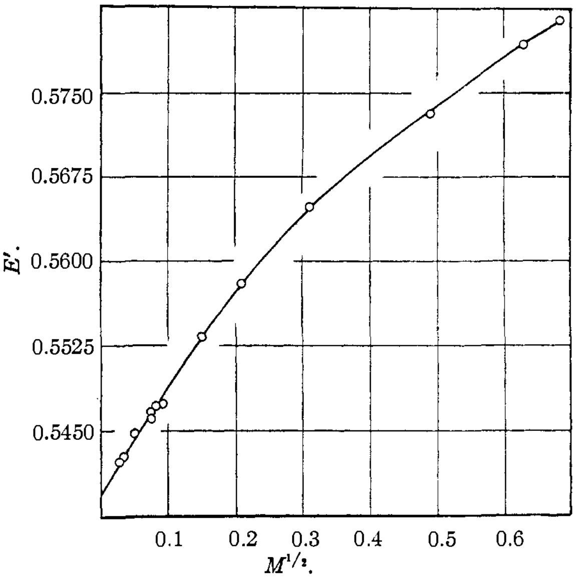

Fig. 2.—The extrapolation method for determining E_0 for the mercury–mercurous sulfate electrode in methanol at 25°.

The stoichiometric activity coefficient γ' is defined as the product of the mean, molal activity coefficient $\gamma_\pm$ and the degree of dissociation α. For very dilute solutions the difference between $\gamma_\pm$ and the mean molar activity coefficient $f_\pm$ is negligible. One may also assume that molarity C equals the product of molality and density of solvent d. Thus the dilution law may be written as

$$\frac{md(\gamma')^2}{1 - \alpha} = K \qquad (13)$$

where K is the thermodynamic ionization constant. By adopting the values of K that were reported by Kanning, Byrne and Bobalek,[7] and using the values of α' cited in Table II, it is possible to compute approximations of α and $f_\pm$.

The limiting Debye–Hückel equation, namely

$$-\log f_\pm = A(C\alpha)^{1/2} \qquad (14)$$

predicts that a plot of $-\log f_\pm$ *versus* $(C\alpha)^{1/2}$ will be a straight line in the dilute concentration range with slope equal to A. Figure 3 is such a plot for data at 25°, where the theoretical slope A (1.99) is shown as the broken line. Figure 3 reveals that the experimental results approach the theoretical predictions for very dilute solutions. The same conclusion is deduced from the data at all the temperatures of measurement, except that the agreement of the theoretical and experimental values seems to improve slightly with increasing temperature in the range of 20–35°.

Following the procedure of LaMer and associates[14,15,16] the Gibbs–Helmholtz equation for the cell under discussion may be written in the form

$$-\Delta H = 2F\left(E' - T\left(\frac{\partial E'}{\partial T}\right)\right) \qquad (15)$$

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[14] LaMer and Parks, THIS JOURNAL, **53**, 2040 (1931).

[15] LaMer and Cowperthwaite, *ibid.*, **55**, 1004 (1933).

[16] Cowperthwaite, LaMer and Barksdale, *ibid.*, **56**, 544 (1934).

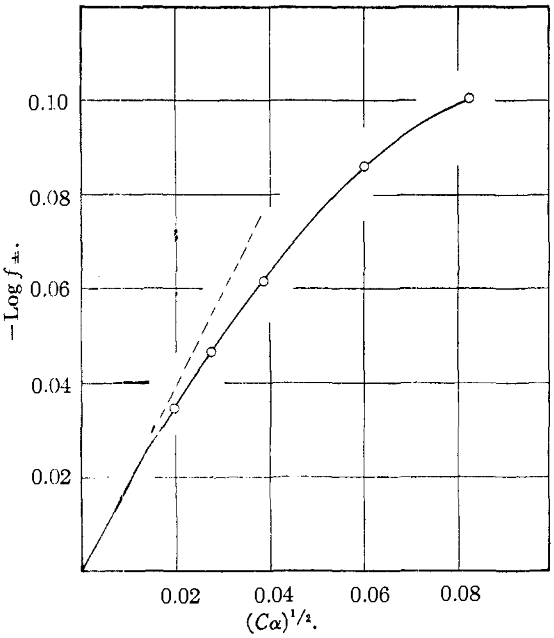

Fig. 3.—Comparison of the experimental values of the activity coefficient with the predictions of the Debye–Hückel equation for sulfuric acid in methanol at 25°.

Since the sulfuric acid is the only reactant of variable activity, $-\Delta H$ equals $\overline{H}_2$, the partial molal heat content of sulfuric acid in the solution. If the conventional assumption is made that the molal heat contents of pure solvent and pure solute are equal to zero, and the infinitely dilute solution chosen as the reference state, one may write

$$\overline{L}_2 = \overline{H}_2 - \overline{H}_2^0$$

where $\overline{H}_2^0$ is the partial molal heat content of the infinitely dilute solution and $\overline{L}_2$ is the *relative* partial molal heat content or, for the present cell, the partial molal heat of dilution for sulfuric acid solutions in methanol.

In order to calculate heats of dilution as indicated above, the temperature coefficients of E' values are required. It may be assumed that E'_t for each concentration (t is any temperature between 20 and 35°) can be represented by the equation

$$E'_t = E'_{20°} + a(t - 20) + b(t - 20)^2 \qquad (16)$$

The constants for this equation were evaluated for rounded concentrations by the method of least squares. These are listed in Table III. Temperature coefficients may be obtained by differentiating this equation with respect to $(t-20)$.

TABLE III

CONSTANTS FOR THE EMPIRICAL EQUATION $E'_t = E'_{20°} + a(t - 20) + b(t - 20)^2$

Molality	$E'_{20°}$	$a \times 10^4$	$b \times 10^5$
0.0000	0.5443	−10.9067	1.7229
.0005	.5463	−10.3200	1.760
.0010	.5471	−10.090	1.766
.002	.5483	− 9.757	1.772
.005	.5505	− 9.197	1.820
.010	.5529	− 8.740	1.946
.020	.5561	− 8.290	2.160
.050	.5621	− 8.043	2.771
.100	.5679	− 8.226	3.422
.200	.5746	− 8.053	3.631

Since at this time the authors do not intend to advance any theoretical discussion of thermochemical data, the actual values for the partial molal heats of dilution of sulfuric acid in methanol have not been listed. However, such results can be calculated readily from the data that are cited by following the procedure that has been indicated.

Summary

Measurements were made on the cell

(Pt) H_2-H_2SO_4 in methanol-Hg_2SO_4 Hg

Standard electrode potentials were determined at 20, 25, 30 and 35°. The respective values found are 0.5443, 0.5392, 0.5351 and 0.5318 volt, and the precision of the determination of these values is estimated to be ±0.0005 volt.

Evidence is presented supporting the conclusion that sulfuric acid in methanol is essentially an incompletely dissociated uni-univalent acid. Moreover, it was demonstrated that the data of this investigation and of earlier electrical conductivity measurements are mutually consistent in demonstrating the validity of the Debye–Hückel equation for very dilute solutions of this electrolyte.

Data are listed and a method is presented which permits the calculations of partial molal heats of dilution for solutions of sulfuric acid in methanol in the temperature range of 20–35°.

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