[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY]

The Conductivity of Sulfuric Acid in Methanol at 25°[1]

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Some preliminary investigations have been reported concerning the application of the electromotive force method of MacInnes and Beattie to the determination of transference numbers of sulfuric acid in methanol.[5] The results appeared to indicate that the interpretation of the data in terms of analogies with closely parallel studies of aqueous sulfuric acid solutions would lead to values for transference numbers that seemed reasonable. However, the assumption concerning the complete dissociation of sulfuric acid, although very useful in explaining the properties of dilute aqueous solutions, seemed to lead to some inconsistencies when applied to the interpretation of the data in methanol solutions. It seems probable that analogies based on the properties of aqueous sulfuric acid solutions can be applied only to a very limited extent to solutions in a solvent that is even as closely related to water as is methanol. Unfortunately, the question of the dissociation of sulfuric acid was not subject to check by the experimental techniques of the particular types of electromotive force measurements that have been reported. Therefore, it seemed of interest to anticipate any extension of electromotive force studies by obtaining some fundamental conductance data which may lead to a better understanding of the dissociation properties of sulfuric acid in that solvent.

Experimental

Materials.—A pure grade of synthetic methanol was freed of reducing impurities and subjected to a preliminary drying according to the method of Kanning and Campbell.[6] Additional drying was effected by repeated distillations from magnesium. After two to four such distillations only a slight turbidity was produced by dissolving 10 g. of magnesium per liter of alcohol. The methanol recovered from the last distillation from magnesium was refluxed for several hours over pulverized anhydrous copper sulfate, and then distilled slowly, using a two meter fractionating column. The first and last fractions of the distillate were discarded. The middle fraction had a specific conductivity of 0.09–0.11 $\times 10^{-6}$ ohm^{-1}, which compares favorably with the minimum values of the specific conductivity that are reported in the literature.[7]

Pure sulfuric acid was prepared in the manner described by Hantzsch.[8] The stock materials were Baker Special grades of 98% sulfuric acid and fuming sulfuric acid (30% excess sulfur trioxide). The 98% acid was titrated to a maximum freezing point in a Beckmann apparatus with a 10% solution of sulfur trioxide in sulfuric acid. The maximum freezing point of the 100% sulfuric acid thus prepared was 10.50 ± 0.05°. Hantzsch reports a melting point of 10.46 ± 0.02° for pure sulfuric acid.[8] The product thus obtained was twice again purified by partial freezing and decantation of the residual uncrystallized sulfuric acid. This operation caused no further change in the freezing point. The acid was transferred into glass-stoppered bottles and stored in a phosphorus pentoxide desiccator. Consistent conductivity measurements were obtained for solutions prepared from three independently purified stocks of sulfuric acid.

A pure C. P. grade of potassium chloride was recrystallized four times from conductivity water, dried, fused in a platinum crucible over the direct flame of a Meker burner, and was poured into a platinum dish. The salt was pulverized in an agate mortar while still hot, and stored in glass-stoppered bottles in a desiccator. A saturated solution of the salt reacted neutral to phenolphthalein, and showed negative tests for nitrates (with diphenylbenzidine) and for sulfates (with barium chloride). Standard solutions made up from samples of potassium chloride prepared by two separate purifications had the same specific conductivities.

The water used in the preparation of standard solutions was distilled successively from acid permanganate and Nessler solution. A third distillation was made using a block tin condenser and a quartz receiving flask. The freshly prepared water had a specific conductivity of 0.3–0.4 $\times 10^{-6}$. After a short exposure to the laboratory atmosphere, the conductivity increased to 1.0–1.2 $\times 10^{-6}$. The standard potassium chloride solutions were prepared from water of the higher but more stable conductivity, and the normal additive solvent correction was applied to the data.

Apparatus and Procedure.—The bridge for the measurement of the conductivity of the solutions was constructed by Leeds and Northrup in accord with the principles discussed by Jones and Josephs.[9] The oscillator and amplifier were the standard type supplied by Leeds and Northrup as a complement to the bridge assembly. The man-

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(5) Kanning and Waltz, THIS JOURNAL, **63**, 2676 (1941).

(6) Kanning and Campbell, *ibid.*, **64**, 517 (1942).

(7) Hartley and Raikes, *J. Chem. Soc.*, **127**, 524 (1925); Carrara, *Gazz. chim. ital.*, **26**, I, 119 (1896).

(8) Hantzsch, *Z. physik. Chem.*, **29**, 130 (1925).

(9) Jones and Josephs, THIS JOURNAL, **50**, 1049 (1928).

ner of operating the apparatus is quite completely described elsewhere.[10] A cathode ray oscillograph of the type described by Jones and co-workers[11] replaced the telephones as a null point indicating device. The resistance coils of the bridge were standardized against a set of resistances calibrated by the Bureau of Standards.

The measurements were performed with the cells immersed in a constant temperature oil-bath. The thermostat, when properly adjusted, maintained a temperature which deviated from constancy to an extent that could not be detected by a Beckmann thermometer. The temperature of the bath was checked by means of two Bureau of Standards calibrated thermometers with scales permitting readings to a precision of ±0.003°. The temperature control of the bath was somewhat better than was the certainty of knowledge of the absolute value of the temperature.

Three cells were used successfully for the concentration range for which measurements are reported. Two of the cells were of the type described by Jones and Bollinger[12]; the cell constants were 5.8293 and 0.63741. The cells were constructed of Pyrex glass except for a small amount of uranium and lithium glass at the Pyrex–platinum seal. The non-Pyrex glass appeared to be soluble enough to make somewhat uncertain the resistance measurements on dilute aqueous solutions. This effect was less noticeable in methanol solutions than in water; however, it was still significant enough to handicap the use of these cells for measurements on very dilute solutions. The third cell used for measurements on solutions more dilute than 0.0005 molar was constructed entirely of Pyrex glass, and it showed none of the effects that are attributed to the solubility of the glass in the other two cells. The cell was a modification of the type described by Jones and Bollinger[12] and had a cell constant of 0.30995.[13] This cell was designed so as to permit the use of a technique that made possible consistent measurements on very dilute solutions. It was noted that the conductivity of dilute solutions decreased irregularly with time. Approximately the same initial readings were obtained after duplicate fillings of the ordinary type of cell with the same stock solution. This effect was produced even by flushing the same portion of the solution in and out of the cell. Such behavior was more pronounced for several days after the electrodes had been cleaned.[14] This difficulty of drifting resistance values was overcome by the following modification in the design and technique of use of the cell. One filling tube of the ordinary type of cell was replaced by a 2-cm. length of 10-mm. glass tubing which was connected to the bottom of a glass stoppered 250-ml. round-bottom flask. The second filling tube was brought up vertically to the height of the cap on the flask and then bent over and downward and joined to the flask just below the neck. The cell could be tilted in the bath so that the cell solution emptied into and mixed with the same solution in the reservoir. The solution was then allowed to drain back into the cell. The resistance dropped to a lower value after each such exchange of the cell solution with the solution in the reservoir. This process was repeated (two to four times) until successive repetitions of this procedure no longer resulted in a change of the resistance reading of the cell. This technique yielded stable resistance readings that agreed to 0.05% when the cell and reservoir were refilled several times with the same stock solution. Consistent data were obtained on solutions of almost the same concentration, but prepared of different stocks of reagents. The consistency of the results obtained by this technique seems to justify its application even though the reasons for the trouble or the remedy are not clearly understood. These difficulties may be of the same nature as those observed by Shedlovsky in his work on dilute aqueous solutions.[15]

The electrodes were not platinized. For the dilute solutions measured, a light platinization seemed to have no advantage over the bright electrodes, whereas a heavier platinization appeared to influence irregular decreasing drifts of the resistance readings for methanol solutions.

Measurements were made at alternating current frequencies of 500, 1000 and 2000 cycles per sec. The difference between the resistance readings at the two higher frequencies was usually less than 0.02% in methanol solutions and about 0.03% in the most concentrated potassium chloride solutions used in the determination of the cell constants. The slightly lower value of the resistance at the higher frequency was accepted as being the better approximation of the true value. The cell described for the measurements on the most dilute solutions was particularly satisfactory; the capacitance necessary to balance that of the cell was usually less than 100$\mu\mu$f. and the variation of the resistance values at 1000 and 2000 cycles was less than 0.01% for all measurements reported at concentrations lower than 0.001 molar. For concentrations greater than 0.0005 molar, the data reported are based on the mean of resistance measurements made using at least two of the cells described above.

The constant of the cell of the higher resistance was determined using a standard 0.01 demal aqueous potassium chloride solution having a specific conductivity of 0.0017088 ohm^{-1} at 25°.[16] The results of three separate determinations of the cell constant, using separately purified samples of reagents, agreed to ±0.002%. The constants of the two cells of lower resistance were determined by comparison of the cell resistance ratios when all three cells were filled with a common solution. Ten dilute aqueous potassium chloride solutions of varying composition were used. The cell constants thus obtained agreed to ±0.002%. The constancy of the resistance ratios of the cells was checked throughout the progress of the work.

The solutions were prepared by weighing both the solute and solvent. The concentration was computed from the molality on the basis of the assumption that the density of the dilute solutions was approximately equal to the den-

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(10) Dike, *Rev. Sci. Instruments*, **2**, 379 (1931).

(11) Jones, Mysels and Juda, THIS JOURNAL, **62**, 2919 (1940).

(12) Jones and Bollinger, *ibid.*, **53**, 411 (1931).

(13) The dimensions are the following: cell capacity, 30 ml.; cell diameter, 3 cm.; diameter of electrodes, 2.4 cm.; distance between electrodes, 2 cm.

(14) The cleaning was accomplished by allowing hot chromic acid solution to stand in the cells for an hour, rinsing thoroughly with distilled water and then steaming for several hours. The cells were filled with conductivity water and allowed to stand for several days with frequent refillings with hot water. The cells were filled with pure methanol at least one day before measurements were made on non-aqueous solutions.

(15) Shedlovsky, THIS JOURNAL, **54**, 1411 (1932).

(16) Jones and Bradshaw, *ibid.*, **55**, 1780 (1933).

sity of the pure solvent. Density determinations by the method of Parker and Parker[17] seemed to substantiate the validity of this assumption for solutions more dilute than 0.005 molar. The differences of the density of the solutions from that of the pure solvent, as measured by this technique, were not sufficiently outside of the range of experimental error to have any significance. In view of the other experimental limitations of this work, little would be gained by a greater refinement of the density determinations. The figure determined for the density of the pure solvent is 0.78656. This is lower than the value of 0.78662 of the "International Critical Tables"[18] and is in better agreement with the value of 0.78651 given by Lund and Bjerrum[19] and the value of 0.786525 of Jones and Fornwalt.[20] The approximate equation of Kanning and Waltz[5] was used to compute the molarity of the two most concentrated solutions for which measurements are reported. Density measurements indicate that this equation is in error by less than 0.1% for the two higher concentrations. The density data are not cited because they were not checked by a sufficient number of experiments. For reasons now to be discussed, little faith is to be held that determinations of the molar conductance at concentrations greater than 0.006 molar are correct to more than 1%. Since the data in the more concentrated solutions are to be given very limited consideration, no effort was made at this time to substantiate the density determination more precisely in the higher concentration range.

The resistance readings of the methanol solutions of concentrations greater than 0.003 molar drifted indefinitely to lower values. The observed resistance was a linear function of time and apparently was not caused by any electrode effects. The initial resistance reading taken after refilling the cell with the same solution could be predicted to 0.2% by extrapolation of the resistance–time curve of the first series of measurements to the time of the measurement on the duplicate solution. No noticeable difference was observed if the solutions were stored at 0° or at room temperature during the one to two hour period before refilling the cell. Duplicate measurements of the specific conductivity at different time intervals were obtained with different cells. The rate of change of conductivity was about 0.01% per minute at concentrations of about 0.003 molar and increased to about 0.05% per minute at concentrations of about 0.02 molar. At lower concentrations, the initiation of the resistance drift was preceded by a time lag during which stable measurements were possible. Except for small temperature fluctuations, the initial resistance readings at concentrations near 0.002 molar were stable for more than a half an hour before they began to drift to lower values at a much slower rate of about 0.003% per minute. The resistance–time curve was no longer regular. Solutions of concentration lower than 0.001 molar yielded stable readings that could be duplicated with a precision of 0.04% after successive refillings of the cells over a period of more than two hours. The molar conductance of solutions at concentrations greater than 0.003 molar are computed on the basis of resistance values obtained by extrapolation of the resistance–time curves to the time of preparation of the solutions; consequently, these data at the higher concentration are somewhat more uncertain than those for the more dilute solutions.

Solutions prepared by dilution of stock solutions of concentrations exceeding 0.005 molar did not give acceptable results. Greater consistency was obtained by directly preparing stock solutions of a concentration less than 0.003 molar and making weight dilutions of these already dilute stock solutions.

The sulfuric acid was weighed as rapidly as possible in a small tightly sealed weighing bottle on a microbalance, and the bottle was then opened and dropped into a flask containing a weighed amount of solvent. The flask containing the solution was connected to the cell filling tube by ground-glass joint adapters and the cell was filled by tilting the apparatus. Under the low humidity conditions prevailing in the laboratory, it was found that the tedious precautions of protecting the solution from atmospheric moisture during the filling process did nothing toward improving the results if less than two minutes were taken to rinse and fill the cell.

An additional difficulty manifested itself in the instability of the values of the specific conductance of the pure solvent. Within an interval of two hours of standing in a closed Pyrex flask, the specific conductance increased from the initial values of 0.09–0.11 × 10^{-6} to 0.2–0.3 × 10^{-6}. After eight hours, it usually increased to 0.6–0.8 × 10^{-6}. Since no definite solvent correction was to be applied to the data, it was found to be desirable to prepare the solutions using as pure a sample of solvent as could be obtained. Consequently, the solutions were prepared and the measurements were completed within one hour after the required quantity of alcohol was collected from the final distillation. The consistency of the measurements depended to a considerable extent upon careful adherence to this practice.

Data and Results

The data obtained for the conductivity of sulfuric acid in methanol are summarized in Table I, where C represents the concentration in moles per liter, and Λ_m is the molar conductance.

TABLE I

CONDUCTIVITY OF SULFURIC ACID IN METHANOL AT 25°

$C \times 10^4$	Λ_m^a	Λ'_0	$C \times 10^4$	Λ_m	Λ'
0.6006	183.6	186.1	11.132	170.4	181.1
1.0402	182.5	185.8	23.310	162.8	178.0
1.9859	180.7	185.3	24.322	160.7	176.0
2.3872	180.3	185.2	25.376	160.7	176.4
2.5940	179.3	184.5	30.427	157.5	174.6
5.2481	175.4	182.7	41.918	152.0	171.9
8.1891	172.8	181.9	93.879	138.8	168.4
9.7002	170.7	180.6	210.66	128.3	173.2

[a] The equivalent conductance Λ is considered to be identical with molar conductance Λ_m.

An inspection of the data will make apparent the fact that the situation of almost complete dissociation of sulfuric acid in water is not duplicated in methanol solutions. Reliable experi-

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(17) Parker and Parker, *J. Phys. Chem.*, **29**, 130 (1925).

(18) "Int. Crit. Tables," Vol. III, p. 27.

(19) Lund and Bjerrum, *Ber.*, **64B**, 210 (1931).

(20) Jones and Fornwalt, THIS JOURNAL, **60**, 1684 (1938).

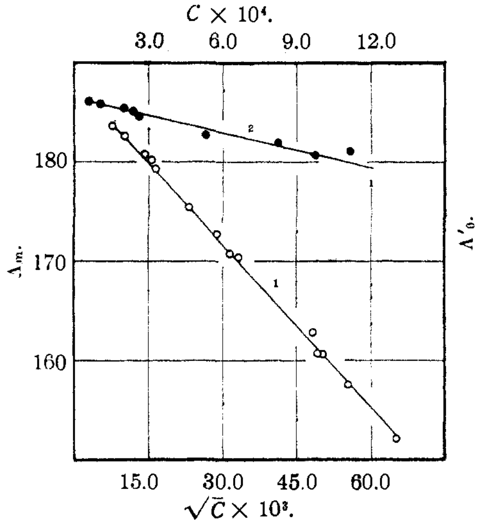

Fig. 1.—Curve 1 is a plot of Λ_m against $\sqrt{C}$. Curve 2 is a plot of Λ'_0 against C. (The upper and right-hand scales apply to Curve 2.) Since sulfuric acid is considered as a univalent electrolyte, the terms Λ_m and Λ are identical.

mental data[21] on the halogen acids and their alkali salts yield a reasonable estimate of 142 for the limiting equivalent conductance of the solvated proton in methanol. Unfortunately, no experimental data are available concerning the equivalent conductances of the sulfate and bisulfate ions. However, assuming the correctness of the value given for the solvated proton, it would be difficult to conceive of values of the molar conductance for nearly completely dissociated sulfuric acid which could be as low as the experimental values quoted at high dilutions.

Moreover, the curve drawn by plotting the molar conductance as a function of the square root of the concentration (Fig. 1) appears to be linear in the concentration range lower than 0.002 molar. This manner of variation of the conductance with concentration seems to be in accord with the behavior that is characteristic of a uni-univalent electrolyte. The occurrence of such a property is not too surprising. In general, moderately strong acids in water are about one hundred thousand times weaker acids in methanol.[22] The bisulfate ion in water has a dissociation constant 0.012,[23] and in accord with the expectations that may be deduced from a comparison of ionization constant ratios of other acids in water and methanol, the dissociation constant of the bisulfate ion in methanol should not exceed 10^{-7}. Unless exactly compensated by interionic attraction effects, any greater amount of secondary dissociation should influence positive deviations from linearity of the Kohlrausch square root plot in the concentration range of interest. On the contrary it seems as though any deviations from linearity that occur are manifested in the tendency for the curve to develop a slight downward curvature at the higher dilutions. This seems to be more of what may be expected if sulfuric acid behaves as a strong but incompletely dissociated uni-univalent electrolyte.[24] It would seem of interest to examine the question further on the basis of the assumption that the secondary dissociation of sulfuric acid is not significant enough to obscure its essential properties as a uni-univalent electrolyte in methanol solutions. Consistent results obtained by such treatment should additionally confirm the assumption of the small value of the secondary dissociation constant.

In order to simplify the notation in the following discussion, the terms equivalent conductance Λ and equivalent concentration C will be considered to be identical with the molar conductance Λ_m and the molar concentration m.

The curve obtained by plotting the equivalent conductance as a function of the square root of concentration is linear. Extrapolation to infinite dilution by the method of least squares yields a value of 187.8 for the limiting equivalent conductance Λ_0 and a value of -529.4 for the slope in the concentration range less than 0.002 molar. This approximate value of 187.8 for Λ_0 can be used to calculate a reasonable estimate of the theoretical slope by use of the Onsager equation

$$\Lambda = \Lambda_0 - (\theta\Lambda_0 + \sigma)C^{1/2} \qquad (1)$$

For methyl alcohol at 25°, the constants θ and σ based on values of 31.5 for the dielectric constant[25] and 0.0054 poise for the viscosity[26] are, respectively, 0.892 and 155.0. Hence the theoretical value of the slope is -323. The difference between the theoretical and experimental slopes is about 40%. No reasonable change in the approximation of Λ_0 can produce much better agreement.

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[21] Murray, Rust, and Hartley, *Proc. Roy. Soc.* (London), **A126**, 84 (1929); Hartley and Raikes, *Trans. Faraday Soc.*, **23**, 393 (1927); MacInnes, "Principles of Electrochemistry," Reinhold Publishing Corp., New York, N. Y., 1939, p. 365.

[22] Davies, "Conductivity of Solutions," John Wiley and Sons, Inc., New York, N. Y., 1933, p. 114.

[23] Sherrill and Noyes, THIS JOURNAL, **48**, 1861 (1926).

[24] Davies, *loc. cit.*, p. 96.

[25] Akerlof, *ibid.*, **54**, 4125 (1932).

[26] Hartley and Raikes, *J. Chem. Soc.*, **127**, 524 (1925).

It is generally recognized that conformity to the square root rule is not necessarily a criterion of complete dissociation. This fact finds examples in such systems as cyanoacetic acid in water, sodium iodide in acetophenone, and the halogen acids in ethanol.[21] In all such instances, the values of Λ_0' computed by using the experimental data and theoretical constants in equation (1) vary linearly with the concentration; however, the values of Λ_0' decrease instead of increase with rising concentration as is the usual situation with most completely dissociated electrolytes. The values of Λ_0' for sulfuric acid in methanol are listed in the third column of Table I. Curve 2 of Fig. 1 shows that the variation of Λ_0' with the concentration is linear, as is predicted by the equation proposed by Shedlovsky,[27] namely

$$\Lambda_0' = \Lambda_0 + BC \tag{2}$$

The curve intersects the zero concentration ordinate at a value of Λ_0 equal to 186.4.

The Onsager equation can be written so as to apply only to the dissociated fraction of the electrolyte, namely

$$\Lambda_e = \Lambda_0 - a(\alpha C)^{1/2} \tag{3}$$

where Λ_e is the equivalent conductance corrected for interionic attraction effects at the concentration C and the degree of dissociation α is defined as the ratio of the observed equivalent conductance Λ and Λ_e at the concentration C. If a good approximation of the limiting equivalent conductance is known, such can be used in the equation as a fixed value for Λ_0 and also as the initial value of a series of approximations of Λ_e.[21] The calculation can be repeated using the newly derived values of Λ_e to determine a better value of α until a repetition of the computation no longer changes the result. Usually a good approximation of Λ_0 can be estimated from the additivity of the individual ionic conductances deduced from data on solutions of electrolytes that are known to be completely dissociated. Unfortunately, because of the technical difficulties of making precise measurements on solutions of the very sparingly soluble alkali sulfates and bisulfates, such desirable data were unavailable in this instance. However, the series of approximations indicated above were performed using 186.4 as the best available value of Λ_0. Table II summarizes the values of the final approximation of Λ_e and α, and of the classical dissociation constant K'.

TABLE II

DATA FOR PRIMARY DISSOCIATION OF SULFURIC ACID IN METHANOL AT 25°

$C \times 10^4$	Λ	Λ_e	α	K'	$f_\pm$	$Kf_\pm{}^2$
0.6006	183.6	183.9	0.998	0.037	0.965	0.034
1.0000	182.5	183.2	.996	.026	.957	.024
2.0000	180.3	181.9	.991	.023	.938	.020
5.0000	175.9	179.4	.981	.025	.905	.020
10.000	171.0	176.4	.969	.031	.867	.023
20.000	164.1	172.4	.952	.038	.819	.025

These data, except for the most dilute solution measured, are reported at even concentrations. The experimental values for Λ at even concentrations are computed from the empirical equation

$$\Lambda = 187.8 - 529.4C^{1/2} \tag{4}$$

The accuracy of these approximations is probably as good as is the general precision of the measurements. The true thermodynamic dissociation constant was calculated from the relation

$$K = K'f_\pm^2 \tag{5}$$

Values for the mean ionic activity coefficients $f_\pm$ were calculated from the Debye–Hückel limiting law

$$-\log f = A(\alpha C)^{1/2} \tag{6}$$

The theoretical value of A at 25°, based on a value of 31.5 for the dielectric constant,[22] is 1.99. The calculated values of $f_\pm$ and of the thermodynamic dissociation constant K' are listed in Table II. The application of the Debye–Hückel limiting law appears to improve the constancy of the values of the dissociation constants. Errors of 0.1% in α can lead to errors of 25% in the calculated values of K. In view of the uncertainty of the value of Λ_0 and considering the serious effect of small experimental errors on the calculated result, the agreement of the constants may be considered to be satisfactory.[24] The trend of the constant to rise with increasing concentration conforms to the usual expectations[28] except at the lower concentrations where the effects of secondary dissociation may become more noticeable.

Another system of calculations that involves the method of extrapolation of Fuoss and Kraus[29] may be used to approximate the quantities $f_\pm$,

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(27) A similar equation is deduced by Onsager [*Physik. Z.*, **28**, 277 (1927)] from the mass action law for electrolytes that are nearly completely dissociated. The constant B is identified with the ratio Λ_0/K. The slope of the curve 2 in Fig. 1 is −5692 and the intercept Λ_0 is 186.4; this would fix a value of 0.0328 for the classical dissociation constant for the primary ionization step.

(28) MacInnes, *loc. cit.*, Chapters 18 and 19.

(29) Fuoss and Kraus, THIS JOURNAL, **55**, 476, 2390 (1933); Fuoss, *ibid.*, **57**, 48 (1935).

K, and Λ_0 for strong, incompletely dissociated electrolytes. This series of approximations involves no assumption concerning the correctness of the initial approximation of Λ_0. This method is based on a combination of the mass action law, the Onsager equation, and Debye–Hückel limiting law, and should apply to this system in the dilute concentration range where the assumptions upon which the computation is based may be expected to be valid. Since this method involves a combination of those considerations already separately discussed, the details will not be repeated. This calculation yielded values of α and $f_\pm$ identical with those obtained from the preceding computations. The linear extrapolation upon which the Fuoss–Kraus method is based yielded an approximation of 186.5 for Λ_0 and a value of 0.029 for K. This is in good agreement with the approximations deduced from previous calculations and tends to prove the correctness of the estimate of Λ_0 selected for the computations that are summarized in Table II.

Obviously, the neglect of the possible interferences of secondary dissociation makes all of these deductions somewhat questionable from the standpoint of providing a rigid interpretation of the properties of sulfuric acid in methanol; however, these considerations serve to illustrate that, at most measurable concentrations, the solutions of sulfuric acid do not markedly deviate from the properties expected of a strong univalent electrolyte.

It is unfortunate that technical difficulties of the measurements have not permitted, up to this time, experimental work of a precision comparable to that obtained by modern methods on aqueous solutions. Apart from the fact that consistent and reproducible measurements are limited to only very dilute solutions, the other handicaps characteristic of most non-aqueous solutions studies are very evident. Probably the major difficulties are associated with the purification of the solvent. The predominant impurity is water. It has been demonstrated[30] that the additions of 0.01% of water in the alcohols diminishes the conductivity of acids about 1%. Similar effects were noted in this study. The possibilities exist that traces of ammonia may have been introduced into the solvent as a result of the drying process. Since the mobility of the ammonium ion is less than that of the solvated proton, such an impurity can have an undesirable effect on the precision of the measurements. Wynne-Jones[31] has reviewed several methods for correcting the observed values of the conductivity in order to compensate for rather large and comparatively constant quantities of impurities in the solvent. An attempt at such corrections did not improve the consistency of the results of this series of measurements. Whenever the conditions of the solvent that influence the reproducibility of the measurements are too variable to permit any consistent correction, the only alternative that remains is to prepare the solvent with a sufficiently high degree of purity so that the effect of any contamination is small even though not negligible. It is believed that this has largely been achieved in this work. The measurements reported were made on solutions prepared from fifteen different stocks of solvent purified by the method described, and the consistency of the measurements is reasonably satisfactory. In general, the irregular deviations of the points from the best straight line of Fig. 1 are less than 0.1%. Since deviations of this magnitude are possible, the values of the molar conductance are reported to only four significant figures, even though the reproducibility of measurements was usually better than 0.04% on solutions made up by careful duplicate dilutions of a stock solution with the same sample of solvent. The limitations defined by the precision of the experimental work must be considered with greater care than is often necessary in the case of comparable studies on aqueous solutions; however, it is believed that the precision of this work is sufficient to permit the conclusions that are here deduced from the data.

Summary

1. The conductivity of solutions of sulfuric acid in methanol was measured over the concentration range of 0.02107 to 0.00006006 molar. At concentrations lower than 0.002 molar, the molar conductance is a linear function of the square root of the concentration.

2. The experimental results suggest that sulfuric acid in methanol behaves essentially as an incompletely dissociated univalent electrolyte. The data have been interpreted so as to yield an approximate value of 0.029 for the primary dissociation constant of sulfuric acid in methanol at 25°.

Midland, Michigan Received March 25, 1943

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(30) Goldschmidt and Dahl, *Z. physik. Chem.*, **81**, 30 (1913).

(31) Wynne-Jones, *J. Chem. Soc.*, **129**, 630 (1926).