THE VARIATION OF THE PROPERTIES OF ELECTROLYTIC SOLUTIONS WITH DEGREES OF DISSOCIATION[1]

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Methods are now available for the determination of degrees of dissociation of electrolytes, both weak and strong, in solutions of finite concentration. Light absorption and Raman spectral methods contribute to a consistent picture of the composition of concentrated nitric acid solutions. The Debye-Hückel theory, conductance data, kinetic measurements, and the intensities of Raman lines give a reasonably consistent picture of the molecular constitution of aqueous sulfuric acid in solutions of all concentrations.

The data now are sufficient to permit calculation of reasonably satisfactory theoretical curves showing the heats of dilution, apparent molal volumes, and surface tensions of sulfuric acid solutions. Data are insufficient for an entirely satisfactory comparison of computed and experimental values of heat capacities, but the calculations agree as well as can be expected with the uncertain experimental data.

When the Debye-Hückel theory (9) first appeared there were very few data which were sufficiently accurate for testing it. One of the most interesting and significant tests would have been a comparison of the predictions of the theory with precise experimental values of the degrees of dissociation of weak and strong electrolytes. Although the major objective of the vast amount of work that has been done on electrolytic dissociation was the determination of equilibria in solutions of finite concentration, no adequate determinations existed in 1923.

The answers to a number of other fundamental problems of physical chemistry have had to await more knowledge of electrolytic dissociation. Enough information has now accumulated to permit us to make significant progress with one group of problems: namely, the explanation in terms of constitution of variations of familiar properties of electrolytes with concentration and temperature. Some of the most interesting properties—heat of dilution, density, surface tension, and heat capacity—are dealt with in this review.

I. DETERMINATION OF DEGREES OF DISSOCIATION OF ELECTROLYTES

A. Conductance methods

In 1926 two attempts were made to obtain better estimates of degrees of dissociation from conductance data. MacInnes (30) described a method for the investigation of electrolytes of the 1-1 valence type which he has continued to use and develop (31, 33). Prior to 1926 the degree of dissociation had been calcu-

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lated from the ratio of Λ, the equivalent conductance, to Λ_0, the limiting equivalent conductance at infinite dilution. MacInnes employed instead:

$$\alpha = \Lambda/\Lambda_e \tag{1}$$

where Λ_e is the equivalent conductance of only the dissociated part of the electrolyte. Λ_e, in principle, could be determined from Λ_0 by the application of corrections for the influence of interionic forces and other similar effects. In the procedure used by MacInnes, the estimate of Λ_e was based upon the assumption that the sum of the mobilities of the ions of a uni-univalent electrolyte is determined by the total ionic strength. He also used the Debye–Hückel limiting law for estimation of activity coefficients to be used in his calculations. The apparent equilibrium constants obtained with this procedure are essentially constant for acetic acid concentrations ranging as high as 0.0002 mole per liter (32). That concentration is still small, but the improvements in methods and results were definite and important.

In the same year Sherrill and Noyes (55) attacked a somewhat more difficult problem: they dared to work with ions of mixed valence types and at concentrations as high as 0.05 molal. The procedure they developed is, as a result, considerably less general than that of MacInnes. They assumed that the mobility of an ion is the same in two solutions of the same ionic strength, provided the ions in each solution are similar (in structure, valence, etc.). There was little they could do at the time to demonstrate the validity of their method, but apparently they presented their results with considerable confidence. Some of their conclusions concerning sulfuric acid solutions will be compared below with the results of methods developed more recently.

B. The first optical method: light absorption

von Halban and Brüll (13) have recently compared and appraised various methods which have been employed repeatedly in investigations of the dissociation of weak and moderately strong electrolytes. They reiterated earlier conclusions of von Halban and his coworkers that the method of light absorption stands out above the other well-known procedures because it is not highly dependent upon corrections for the influences of solute ions and neutral molecules. The conductance method involved assumptions concerning the variations of ionic mobilities which are large even when solutions are relatively dilute. Freezing-point, vapor pressure, osmotic pressure, and electromotive force methods are affected by assumptions concerning relations of activities and concentration. Some, at least, of the electromotive force methods are marred also by errors due to liquid-junction phenomena for which adequate corrections have not been devised. The molecular extinction coefficient of an absorbing ion, however, is sensibly constant for all ionic strengths less than 0.01. In an earlier paper von Halban and Eisenbrand (14) had observed large changes in the molecular extinction coefficient when the ionic concentrations became very large, but at low concentrations the variations are negligible. With refined optical methods, such as those employed by von Halban and Kortüm (15, 26), a precision as good as

0.01 per cent can be obtained in the measurement of extinction coefficients, and as good as 0.1 per cent in the determination of dissociation constants.

A severe and beautiful test of the Debye–Hückel theory made in 1934 by von Halban and Kortüm (15) is illustrated in figure 1. The ordinates represent the logarithms of the apparent dissociation constant of 2,4-dinitrophenol. The apparent constant (the function calculated directly from concentrations without the aid of activity coefficients) should vary in dilute solutions, as indicated by the straight line whose slope was calculated by means of the Debye–Hückel limiting law. Some of the points at very low concentrations represent solutions containing only the solute, dinitrophenol. Other points show the effects of added neutral salts. The Debye–Hückel limiting law is obeyed almost perfectly for all ionic strengths less than 0.003. It fails, as expected, at higher concentrations, but the principle of ionic strength remains valid to an ionic strength of 0.01. The authors extended their observations to ionic strengths greater than 2.00. In solutions of those high concentrations they observed large specific ion effects. It is not yet possible to determine how much of such an effect is due to influences which alter the degree of dissociation, and how much should be ascribed to variations in the molecular extinction coefficient itself. The usefulness of the method for studying concentrated solutions is therefore limited.

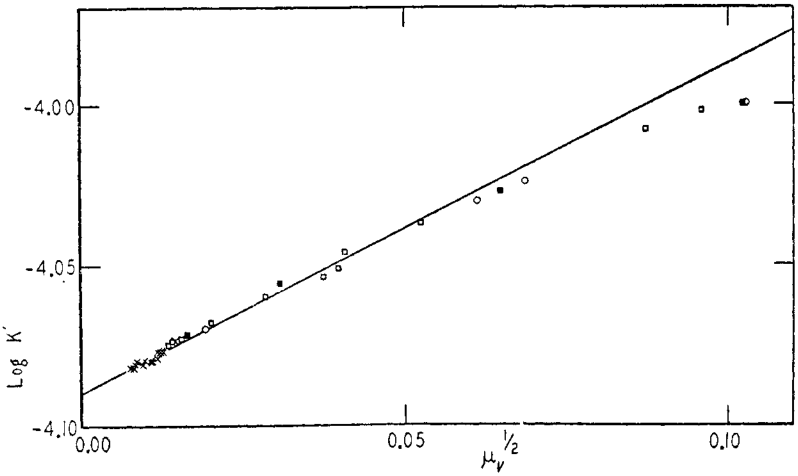

FIG. 1. Logarithm of apparent dissociation constant of 2,4-dinitrophenol at 25°C × indicates acid as sole solute; ○, acid in presence of potassium chloride; □, acid in presence of potassium perchlorate; and ■, acid in presence of sodium chloride. Straight line represents Debye–Hückel limiting slope.

For very dilute solutions, the most important disadvantage of the light absorption method is that it is restricted to equilibria which involve at least one ion or molecule that absorbs light. Though colorless acids or bases can sometimes be studied with the aid of indicators, the procedure is more complex and less accurate.

C. The second optical method: Raman spectra

Another optical method which makes use of Raman radiation has been developing during the last fifteen or twenty years. The method depends upon measurements of the relative intensities (usually determined photographically) of a Raman line produced by exciting radiation supplied by a source of constant strength. Application to investigations of chemical equilibria has usually depended upon the assumption that the intensity of a selected Raman line is proportional to the concentration of the ion or other molecule giving rise to that line. The accuracy of the simple proportionality has been investigated for only a very few substances and inadequately for those. The special attention directed toward nitric acid, however, has resulted in relatively extensive investigations of the line of $\Delta\bar{\nu}$ = 1048 cm.$^{-1}$ arising in solutions of various nitrates. Sodium nitrate solutions have been studied by I. R. Rao (39), Simons (56), and N. R. Rao (41). Simons also studied ammonium nitrate solutions. Relative intensities for these nitrates, taken from the tables of Simons and of N. R. Rao, are shown in figure 2. Simons' measurements of intensities of the 980 cm.$^{-1}$ line from ammonium sulfate solutions are also plotted. The scales used in figure 2 for the intensities are entirely arbitrary. They were chosen, merely to avoid superposition of the lines, so that the slopes would be 0.75, 1.00, and 1.25. Obviously the ratio of intensity to concentration is constant, within the limits of precision of the experimental methods, throughout the ranges of concentration investigated.

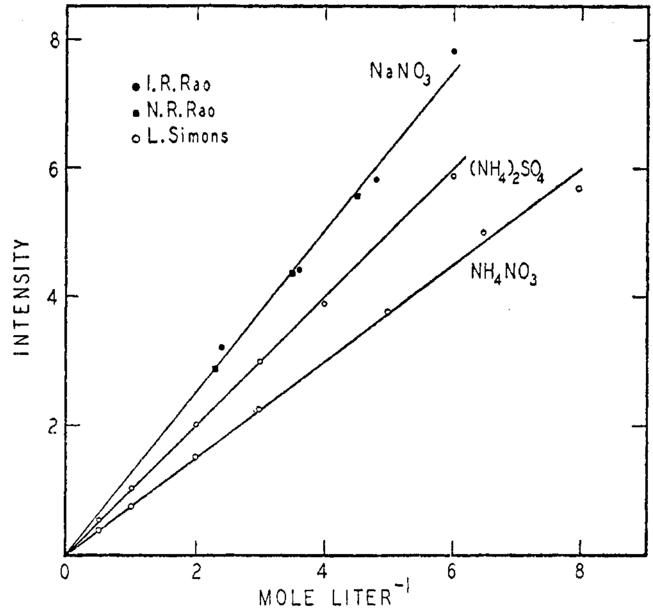

FIG. 2. Relative intensites of Raman lines from solutions of sodium nitrate, ammonium nitrate, and ammonium sulfate. Vertical scales are purely arbitrary.

(1) Nitric acid

The intensity of the Raman line of 1048 cm.$^{-1}$ arising in a concentrated nitric acid solution is not so great as its intensity when produced in a sodium nitrate solution of the same concentration. Moreover, when the concentration of the acid is increased beyond 39 weight per cent the intensity of the 1048 cm.$^{-1}$ line actually decreases. Simultaneously the intensities of other lines (notably the line of 1292 cm.$^{-1}$) characteristic of pure nitric acid become greater.[2]

Redlich and Bigeleisen (46) determined experimentally the concentration of the sodium nitrate solution giving rise to lines of the same intensity as each of several nitric acid solutions. Equating the ratio of the concentrations to the degree of dissociation of the acid, they obtained the results[3] in table 1. From these values they estimated the thermodynamic dissociation constant ($K = 21 \pm 4$). Because the present knowledge of activity coefficients is very limited, the uncertainty in the constant is large. If, however, the assumptions that sodium nitrate is completely dissociated and that the nitrate-ion concentration is the same in solutions giving rise to radiations of equal intensity are accurate, the uncertainties in the degrees of dissociation in table 1 are no greater than those in the experimental work itself.

TABLE 1

Degree of dissociation of nitric acid

C	4.51	6.60	8.90	10.30	11.89	14.23
α	0.823	0.673	0.49	0.39	0.32	0.14

An interesting application of the data in table 1 may be made to the interpretation of the dependence on concentration of the molecular extinction coefficients of nitric acid. von Halban and Eisenbrand (14) have determined curves for light of several wave lengths, showing the variation of the molecular extinction coefficients with concentration. The curves are complex, containing prominent points of inflection, whereas corresponding curves for potassium nitrate (14, 54) are comparatively simple. The points of inflection may readily be ascribed to the rapid rise in the ratio of the concentration of the undissociated nitric acid to that of the nitrate ion as the total concentration increases. From the known degrees of dissociation and the light absorption data for solutions of potassium nitrate and of nitric acid, it is possible to calculate approximately the molecular extinction coefficients of the undissociated nitric acid. The values of the coefficient so calculated exhibit a maximum at about 2800 Å. and then decrease toward zero as the wave length increases beyond 3100 Å.

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[2] The assignment of the various observed frequencies (about 10) in HNO_3 and DNO_3 to the expected modes of vibration of the nitric acid molecule has been successfully carried out (*cf.* Redlich and Nielsen (48)).

[3] Values of α for lower concentrations and references to the extensive earlier literature have been given by Redlich (44). His article is an excellent review of the general problem of the dissociation of strong electrolytes.

Dalmon (7) has measured the absorption of light of 3180 Å. in solutions of nitric acid varying in concentration from 0.8 to 24.6 moles per liter (pure acid). Since undissociated nitric acid does not absorb a significant fraction of light of that wave length, his measurements yield directly approximate relative values of the nitrate-ion concentration and therefore of the degree of dissociation of nitric acid. The results are not strictly comparable to those of Redlich and Bigeleisen, because of the known variations with concentration of the molecular extinction coefficients (14) and because Dalmon's work was done at about 1°C. rather than 26°C. Nevertheless, the fact that Dalmon's data lead to degrees of dissociation almost proportional to those of Redlich and Bigeleisen is an effective argument for the essential correctness of the data shown in table 1.

(2) Other electrolytes

Solutions of only a few other electrolytes have been extensively investigated (19). Iodic acid (42), perchloric acid (47), and trichloroacetic acid (43) have all been shown to be incompletely dissociated strong electrolytes. Mixtures of nitric acid and sulfuric acid and of sulfur trioxide and sulfuric acid have also been studied extensively. For our present purposes, the most interesting system is that of sulfuric acid and water, because its properties exhibit marked variations with temperature and concentration which are more complex and interesting than those of most other electrolytes. These phenomena are due to the favorable magnitude of the dissociation constant of the bisulfate ion.

(3) Sulfuric acid solutions

Figure 3 is a simplified representation of various classes of lines reported for solutions of sulfur trioxide in water. The line of 1271 cm.$^{-1}$ is typical of a group of lines arising in pure sulfur trioxide. That line and about fifteen others are probably due to a non-planar molecule with the formula S_3O_9. Other lines seem to be due to the monomer and, at low temperature, to other polymers (10, 11, 18). As water is added to sulfur trioxide, the intensity of the 1271 cm.$^{-1}$ line drops rapidly while other lines appear and increase in intensity (6, 36). Note the very strong 910 cm.$^{-1}$ line whose intensity rises to a maximum in solutions having the composition $SO_3 \cdot H_2O$. As more water is added the intensity of the 910 cm.$^{-1}$ line drops and a line of 1043 cm.$^{-1}$ appears, increases to a maximum, and finally decreases toward zero (40). Another important line, of 980 cm.$^{-1}$, reaches a maximum in a solution of about 15 mole per cent sulfur trioxide. Another, of 960 cm.$^{-1}$, reaches a maximum at a mole fraction of sulfur trioxide somewhere between 60 and 70 mole per cent (36), but the existing data are too meager to indicate accurately the height or position of the maximum. The line has, however, been studied carefully in solutions more dilute than 50 mole per cent sulfur trioxide (2) and more concentrated than 80 mole per cent (36). In both of these regions the intensity has been shown to be low—nearly zero.

A complex literature has been summarized and greatly simplified in figure 3. Only five typical lines of the many reported are represented. Furthermore, each line is identified by a single wave number. Actually the lines have breadth, i.e., extend over a short range of wave lengths. The shapes of the lines, notably the positions of the maxima, vary with composition (1, 2, 35, 59). Most observers have not worked carefully enough to be forced to take the shape and exact position of the lines into account. The intensities represented in the right half of the diagram were estimated only roughly on a whole number scale from 0 to 10 (36). Fortunately for our purposes, the data shown in the left half of the figure are somewhat more accurate. They were obtained by N. R. Rao (40), using a relatively precise photographic procedure. The intensities he reported are actually the integrated intensities obtained from measurements over the full widths of the lines. He assumed that it is the integrated intensity which is proportional to concentration. His results seem to be accurate to about 10 per cent. Unfortunately, Rao did not report the temperatures of his solutions and presumably did not measure them. He reported only that they were cooled (by water) during the exposures.

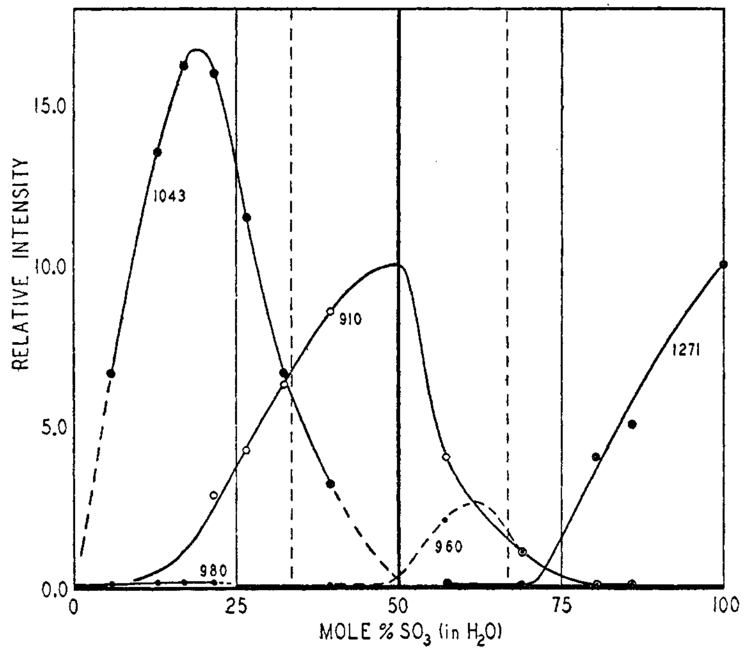

FIG. 3. Intensities of typical Raman lines from solutions of sulfur trioxide and water

Though additional information can yet be derived from more extensive and more precise work, the interpretation of figure 3 seems to be clear. Addition of SO_3 to H_2SO_4 or of H_2O to SO_3 produces pyrosulfuric acid, $H_2S_2O_7$, and the ions $HS_2O_7^-$ and $S_2O_7^{--}$. Presumably the 960 cm.$^{-1}$ line therefore is due to pyrosulfuric acid or one of the products of its dissociation (6). It is interesting to study the decrease in intensity of the 910 cm.$^{-1}$ line as sulfur trioxide is added to sulfuric acid. If we assume that pure sulfuric acid solution contains the one molecular species H_2SO_4, and that 1 mole of it is removed by each gram formula weight of sulfur trioxide added, we can compute the reduction in the concentration of H_2SO_4. These assumptions and the density data of Knietsch (24) lead to the conclusion that the concentration of H_2SO_4 in a solution of 57 mole per cent sulfur trioxide is about 55 per cent of that in pure sulfuric acid. This result is in satisfactory agreement with the 40 per cent indicated on the semiquantitative curve in figure 3. More careful work will probably add considerably to knowledge of the equilibrium in mixtures of sulfur trioxide and water.

The region between 0 and 50 mole per cent sulfur trioxide represents solutions of H_2SO_4 in water. Because he was interested in the relative concentrations of the ions, N. R. Rao measured also the intensities of lines from ammonium sulfate and potassium bisulfate solutions. The strength of the 980 $cm.^{-1}$ line produced in an ammonium sulfate solution and that of the 1043 $cm.^{-1}$ line from a potassium bisulfate solution support the conclusions drawn by Rao and previous workers (2, 35, 59) that the 910, 1043, and 980 $cm.^{-1}$ lines are produced by molecular H_2SO_4, HSO_4^-, and SO_4^{--}, respectively. The usual assumptions (that ammonium sulfate is completely dissociated, and that the ratio of the intensities of the 980 $cm.^{-1}$ line from a sulfuric acid solution and from the ammonium sulfate solution is equal to the ratio of the concentrations of the sulfate ion in the two solutions) lead directly to calculations of the sulfate-ion concentrations in the sulfuric acid and potassium bisulfate solutions[4] (see table 2, column 3).

Subtraction of 0.186 from 3.0 leaves the concentration of bisulfate ion in the 3 molar potassium bisulfate solution. Simple proportion and the measured intensities of the 1043 $cm.^{-1}$ line then yield the concentration of the bisulfate ion in the various sulfuric acid solutions (see column 5). The sum of the SO_4^{--} and HSO_4^- concentrations subtracted from the stoichiometric concentration leaves the concentration of the undissociated H_2SO_4 (column 7). A severe test can be applied to the whole calculation. The 910 $cm.^{-1}$ line should be proportional to the sulfuric acid concentration in column 7. Figure 4 shows that the relation between intensity and the calculated concentration is indeed linear within the limits of error of the photographic technique.

The apparent equilibrium constants K_1' and K_2' were computed for the first and second dissociations directly from the concentrations in table 2. The values of K_2' are compared in figure 5 with the thermodynamic constant determined by Young, Klotz, and Singleterry (22, 57, 61) by means of a light absorption method used with an indicator. The short straight line shows the limiting tangent calculated from the Debye–Hückel theory; the short curved line represents the Debye–Hückel approximation calculated according to the method of Kielland (21) with ion parameters of 9, 4, and 4 Å. for the hydrogen ion, sulfate ion, and bisulfate ion, respectively.

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[4] Rao's assumptions were equivalent to these, but he did not express his results in terms of actual concentrations. The calculations he made were not explained and contained a sufficient number of arithmetic mistakes to make them difficult to follow. They are also awkward for our purposes. All of the calculations described here were based upon the original integrated intensities given in his article. Values similar to those in column 7 were calculated also by De Béthune and Kimball (8).

The upper curve of figure 5 shows values of K_1'. Since the data are insufficient for extrapolation, the curve has been extended arbitrarily to a value of K_1 estimated roughly from the theory of Kossiakoff and Harker (27). The vertical length of the lines represents the uncertainty introduced by a 10 per cent uncertainty in one of the intensity measurements.

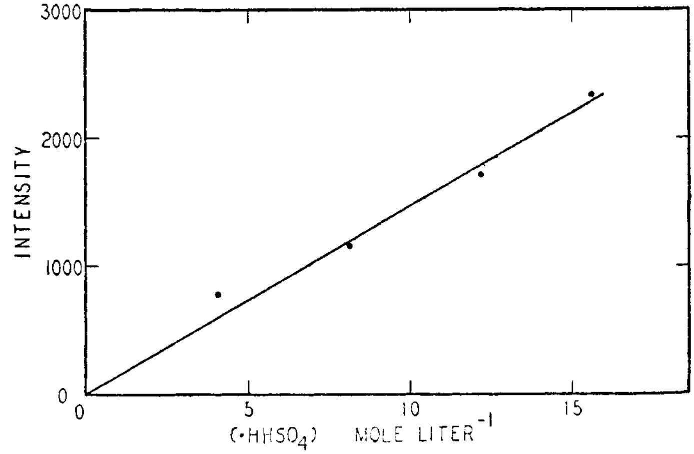

FIG. 4. Intensity of Raman line of 910 cm.$^{-1}$ *versus* concentration of undissociated sulfuric acid calculated by difference.

TABLE 2

Relative intensities of Raman lines and concentrations calculated from them

(1)	(2)	(3)	(4)	(5)	(6)	(7)
(H_2SO_4)	980 cm.$^{-1}$	(SO_4^{--})	1043 cm.$^{-1}$	(HSO_4^-)	910 cm.$^{-1}$	(·$HHSO_4$)
16.9			860	1.28	2330	15.6
14.9			1800	2.68	1700	12.2
12.8			3120	4.65	1150	8.2
10.8	11.8	0.25_2	4350	6.48	765	4.1
8.7	15.2	0.32_5	4412	6.57		1.8
6.8	13.0	0.27_8	3678	5.48		1.0
3.0	6.5	0.13_9	1800	2.68		0.2
$(NH_4)_2SO_4$						
3.0	140.5	(3.00)				
$KHSO_4$						
3.0	8.7	0.18_6	1890	2.81		

The fractions of the solute present as sulfate ions, as bisulfate ions, and as undissociated sulfuric acid are represented in figure 6 by the vertical distances between adjacent lines. The sum of the distances represents unity at all concentrations. In very dilute solutions nearly all of the sulfuric acid is present as sulfate and hydrogen ions; at higher concentrations most of it is bisulfate and hydrogen ions; and in very concentrated solutions most of it is undissociated sulfuric acid.

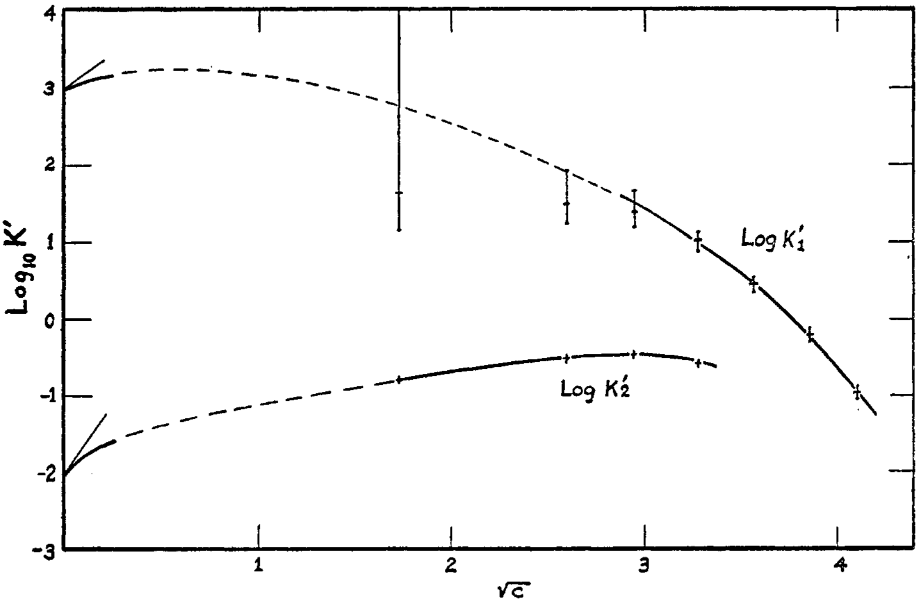

FIG. 5. Apparent dissociation constants K'_1 and K'_2 of sulfuric acid in water. Vertical lines indicate changes that would be produced in K' by alterations of 10 per cent in measured intensities.

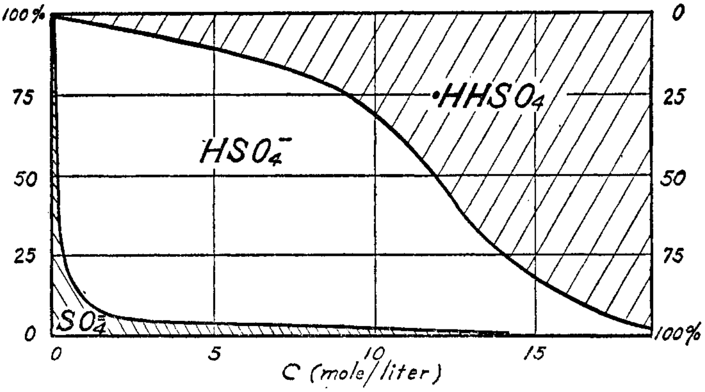

FIG. 6. Fractions of sulfuric acid present as undissociated acid, as bisulfate ion, and as sulfate ion, represented by vertical distances between adjacent lines.

Absolute concentrations may also be computed. In table 3 are shown approximate maximum values of the concentration of the sulfate ion and bisulfate ion, and of the volume and weight ionic strengths. In the bottom line are approximate values of the concentrations of sulfuric acid in which the maxima are attained. The hydrogen-ion concentration reaches a maximum slightly higher, of course, than the maximum (HSO_4^-).

Rao did not investigate solutions more concentrated than 16.9 moles per liter. It is impossible, therefore, to estimate directly from his intensity data the concentration of bisulfate ion in the pure acid. Extrapolation indicates, however, that it is very small. This result is in agreement with the conclusion of Hammett and Deyrup (16) that the bisulfate-ion concentration is about 0.05 mole per liter at 25°C.

For calculations to be described below, it is necessary to calculate degrees of dissociation of the bisulfate ion for a wide range of concentrations and for temperatures varying from 0° to 50°C. Both the dissociation constant and the standard free energy of dissociation vary too rapidly with temperature to be treated as constant. A better approximation is to treat activity coefficients as temperature invariants. To facilitate calculations of equilibria in dilute solutions of sulfuric acid, Bray and Liebhafsky (4) prepared a table of equilibrium quotients which are nearly equivalent to γ_R, the product of the activity coefficients of the hydrogen ion and sulfate ion divided by the activity coefficient of the bisulfate ion.

TABLE 3

Maximum concentrations and maximum ionic strengths

	(SO_4^{--})	(HSO_4^-)	μ_V	μ_W
Maximum value	0.35	6.7	8.0	14.3
Concentration of solution at which maximum occurs	8–10	10	10	11.5

$$\gamma_R = \frac{(\gamma_{H^+})(\gamma_{SO_4^{--}})}{(\gamma_{HSO_4^-})} \tag{2}$$

They based their table upon the degrees of dissociation determined by Sherrill and Noyes (55), supplementing them with kinetic data of their own. Values of γ_R calculated from their paper are shown in figure 7. Shown also are values of γ_R computed from the Raman data of table 2, and two curves calculated from the Debye–Hückel limiting law (labelled D. H. L.) and from the Debye–Hückel approximation (labelled D. H. A). The D. H. A. curve, calculated by the method of Kielland, was based upon ion parameters of 9, 4, and 4 Å. for the hydrogen ion, sulfate ion, and bisulfate ion, respectively.

On the right portion of the plot two series of points are represented: one group calculated from ion concentrations expressed in molarity (moles per liter of solution) and one group expressed in molality (moles per kilogram of solvent). The former are plotted against the square root of the volume ionic strength, μ_V, and the latter *versus* the square root of weight ionic strength, μ_W. By accident, most of the points appear to lie on the same curve. A point lying above the curve at $\sqrt{\mu_V} = 2.6_9$ represents a considerably more concentrated solution than that at $\sqrt{\mu_V} = 2.7_4$, but appears at the left of the latter because of the maximum attained by the volume ionic strength.

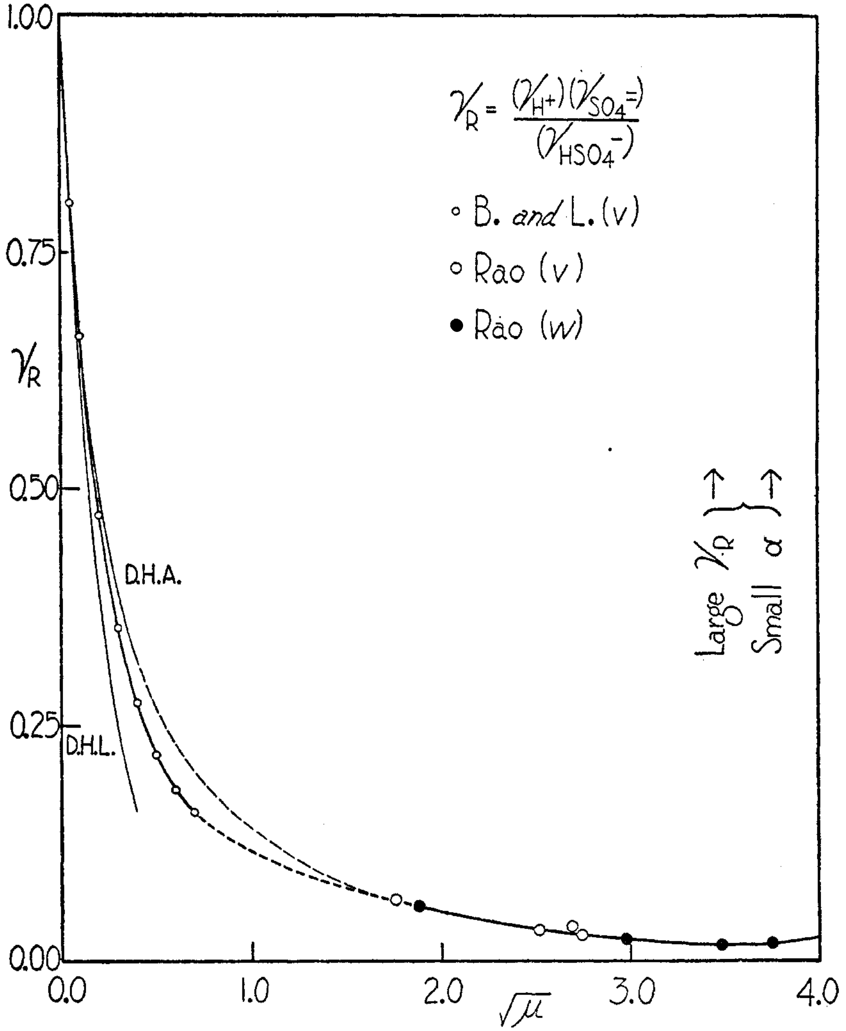

FIG. 7. The activity function γ_R from Raman data, from tables of Bray and Liebhafsky, from the Debye–Hückel limiting law (D. H. L.), and from the Debye–Hückel approximation (D. H. A.).

The agreement between the two sections of the curve is fairly satisfactory and is all that could be expected at the present time. They have been joined by a broken line. Except at very low concentrations, the uncertainties are 10 per cent or more. The Raman data, for example, were treated as 25°C. measurements, although the temperature was not reported. In addition, experimental errors may be as large as 10 per cent. The conductance theory used by Sherrill and Noyes and the methods of Bray and Liebhafsky also may introduce errors of considerable magnitude.

Because of those uncertainties, the experimental curve is probably no more accurate than the theoretical one (D. H. A.) at ionic strengths of 0.2 or less. The latter curve has accordingly been connected by a second broken line with the section representing the Raman data. Within a few years, improvements in the Raman data should make it possible to determine which of the two curves is more accurate. For the present there is little basis for a choice between them for the calculations to follow.

APPLICATION OF ACTIVITY COEFFICIENT CURVE TO ANALYSES OF PROPERTIES OF SOLUTIONS OF SULFURIC ACID

Throughout the following discussions aqueous solutions of sulfuric acid are regarded as mixtures of solvent and three solutes, two of which are completely dissociated. To distinguish the three solutes, the following special notations are used: The formula $H \cdot H \cdot SO_4$ represents that portion of the sulfuric acid which is dissociated into hydrogen ions and sulfate ions; the symbol $H \cdot HSO_4$ denotes the other ionized solute; and $\cdot HHSO_4$ denotes undissociated acid. The concentration of $H \cdot H \cdot SO_4$ is simply the sulfate-ion concentration, and the concentration of $H \cdot HSO_4$ is the concentration of bisulfate ion. The customary formula H_2SO_4 denotes, as usual, the mixture of ionic and molecular species present at equilibrium in a sulfuric acid solution. Obviously:

$$(H_2SO_4) = (H \cdot H \cdot SO_4) + (H \cdot HSO_4) + (\cdot HHSO_4) \qquad (3)$$

where the parentheses as usual indicate the respective concentrations.

The symbol φ stands for any apparent molal quantity (29). φ_H, φ_V, and φ_C denote the apparent molal heat content, apparent molal volume, and apparent molal heat capacity, respectively. φ_C at constant pressure only is needed; hence the subscript p is not used. φ^0 represents φ of a substance in its standard state, and ΔH^0 represents increases in heat content (enthalpy) for reactions involving substances all of which are in their standard states. Thus, φ_V^0 $(H \cdot HSO_4)$ represents the apparent molal volume of $H \cdot HSO_4$ in its standard state. When the difference between φ^0 and φ is written, the appropriate formula is placed below the pair of symbols, instead of in parentheses after each φ.

A. Heat of dilution

Heat is evolved slowly and regularly as a mole of sulfuric acid is diluted from 1 molal toward 0.05 molal (5). As it is diluted beyond 0.05 molal, much larger amounts of heat are evolved. That portion of the dilution curve has been investigated at 25°C. by Lange, Monheim, and Robinson (28; *cf.* 17, p. 439), with whose data our theoretical calculation may be compared.

Since we are concerned with dilute solutions only, we can neglect the presence of $\cdot HHSO_4$. A mole of H_2SO_4 is therefore regarded simply as a mixture of α moles of $H \cdot H \cdot SO_4$ and $1 - \alpha$ moles of $H \cdot HSO_4$. The apparent molal heat content of H_2SO_4 is then $\alpha\varphi_H$ of $H \cdot H \cdot SO_4$ plus $(1 - \alpha)\varphi_H$ of $H \cdot HSO_4$ plus ΔH_M, the heat absorbed during the mixing of hypothetical solutions of $H \cdot H \cdot SO_4$ and $H \cdot HSO_4$.

$$\varphi_H(H_2SO_4) = \alpha\varphi_H(H \cdot H \cdot SO_4) + (1 - \alpha)\varphi_H(H \cdot HSO_4) + \Delta H_M \quad (4)$$

At the concentrations of importance here we shall be able to neglect ΔH_M when the ionic strength of each of the two hypothetical solutions is the same as that of the mixture existing in the real sulfuric acid solution.[5]

The heat of dilution of 1 mole of sulfuric acid from molality m to infinite dilution is the difference between φ_H^0, the standard apparent molal heat content, and φ_H of sulfuric acid at molality m. Thus:

$$\Delta H \text{ (dilution to } m = 0) = \varphi_H^0 - \varphi_H \quad (5)$$

Now φ_H^0 of H_2SO_4 and φ_H^0 of $H \cdot H \cdot SO_4$ are equal, since the conventional standard for each is the infinitely dilute solution.

$$\varphi_H^0(H_2SO_4) = \varphi_H^0(H \cdot H \cdot SO_4) \quad (6)$$

The dilution of sulfuric acid may be thought of as the sum of four hypothetical processes. Consider, for example, the dilution of 1 mole of H_2SO_4 in 0.01 molal solution to infinite dilution. The first step is the separation of a solution containing 1 mole of H_2SO_4 and 10^5 g. of water into two portions containing α mole of $H \cdot H \cdot SO_4$, and $1 - \alpha$ mole of $H \cdot HSO_4$, respectively. The amount of solvent in each is sufficient to make each ionic strength equal to that of the original solution, which is $\mu_W = m(1 + 2\alpha) = 0.01(1 + 2\alpha)$.

$$\begin{array}{c} \text{Solution of } H_2SO_4 \\ \text{and } 10^5 \text{ g. } H_2O \end{array} \rightarrow \begin{array}{c} \text{Solution of} \\ \alpha H \cdot H \cdot SO_4 \text{ and} \\ \dfrac{3\alpha}{1 + 2\alpha} 10^5 \text{ g. } H_2O \end{array} + \begin{array}{c} \text{Solution of} \\ (1 - \alpha) H \cdot HSO_4 \text{ and} \\ \dfrac{(1 - \alpha)}{1 + 2\alpha} 10^5 \text{ g. } H_2O \end{array} \quad (7)$$

ΔH of this separation process is the negative of ΔH_M at constant ionic strength.

Now to each hypothetical solution is added an infinite amount of water:

$$\begin{array}{c} \text{Solution of} \\ \alpha H \cdot H \cdot SO_4 \text{ and} \\ \dfrac{3\alpha}{1 + 2\alpha} 10^5 \text{ g. } H_2O \end{array} + \infty H_2O \rightarrow \begin{array}{c} \text{Solution of} \\ \alpha H \cdot H \cdot SO_4 \text{ and} \\ \infty H_2O \end{array} \quad (8)$$

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[5] A series of investigations now in progress shows that the changes in total volume and in heat content accompanying the mixing of aqueous solutions of electrolytes of the 1-1 valence type are very small when each solution has the same ionic strength as the ternary mixture produced. For solutions as dilute as those involved here, the same is true of the mixing of electrolytes of the 1-1 valence type, e.g., sodium chloride, and of the 1-2 valence type, e.g., potassium sulfate (58). There is some indication, however, in current investigations of the free energy of mixing that changes in volume, heat content, and excess free energy may be even smaller if all of the solutions are of the same normality (49). For the concentrations involved in this calculation, either formulation of the principle leads to essentially the same results.

$$\begin{array}{l}\text{Solution of}\\ (1-\alpha)\mathrm{H\cdot HSO_4}\text{ and}\\ \dfrac{(1-\alpha)}{1+2\alpha}\,10^5\text{ g. }\mathrm{H_2O}\end{array} + \infty\mathrm{H_2O} \rightarrow \begin{array}{l}\text{Solution of}\\ (1-\alpha)\mathrm{H\cdot HSO_4}\text{ and}\\ \infty\mathrm{H_2O}\end{array} \qquad (9)$$

Finally, the $(1 - \alpha)$ mole of infinitely dilute $\mathrm{H\cdot HSO_4}$ is allowed to dissociate:

$$(1-\alpha)\mathrm{H\cdot HSO_4} \rightarrow (1-\alpha)\mathrm{H\cdot H\cdot SO_4} \qquad (10)$$

ΔH of this process is $(1 - \alpha)[\overset{0}{\varphi}_H$ of $\mathrm{H\cdot H\cdot SO_4} - \overset{0}{\varphi}_H$ of $\mathrm{H\cdot HSO_4}]$ which is $(1 - \alpha)$ times the standard heat of dissociation, $\Delta H^0_{\mathrm{Dis}}$, of the bisulfate ion. The heat of dilution of sulfuric acid from any m to $m = 0$ is therefore:

$$\underset{\mathrm{H_2SO_4}}{\overset{0}{\varphi}_H - \varphi_H} = -\Delta H_M + \alpha\underset{\mathrm{H\cdot H\cdot SO_4}}{(\overset{0}{\varphi}_H - \varphi_H)} + (1-\alpha)\underset{\mathrm{H\cdot HSO_4}}{(\overset{0}{\varphi}_H - \varphi_H)} + (1-\alpha)\Delta H^0_{\mathrm{Dis}} \qquad (11)$$

This is the fundamental equation for the theoretical calculation of the heat of dilution of sulfuric acid. The data needed are the hypothetical heat of mixing, the degree of dissociation of the bisulfate ion, the standard heat of dissociation of the ion, and the heats of dilution of the hypothetical solutes $\mathrm{H\cdot H\cdot SO_4}$ and $\mathrm{H\cdot HSO_4}$.

The various terms were evaluated as follows: The hypothetical solutions of $\mathrm{H\cdot H\cdot SO_4}$ and $\mathrm{H\cdot HSO_4}$ formed by an imaginary separation of $\mathrm{H_2SO_4}$ into two parts were presumed to have the ionic strength of the original solution. Hence ΔH_M was taken as zero. For the next term we need the heat of dilution of $\mathrm{H\cdot H\cdot SO_4}$ from a molar concentration equal to one-third of the ionic strength to infinite dilution. The third term is $(1 - \alpha)$ times the heat of dilution of $\mathrm{H\cdot HSO_4}$ from a molarity equal to the ionic strength to infinite dilution. These quantities were computed from the equations for lithium sulfate and sodium chloride given by Young and Seligmann (64). Fortunately, the contribution of these terms is overshadowed by the last, and it is not likely that the error introduced by the substitution of these salts for the hypothetical acids increases appreciably the total error in the calculations.[6] The errors introduced by these and other approximations become smaller as concentration is decreased. The extrapolation aspect of these calculations is probably not affected at all by such approximations.

The standard heat of dissociation was determined from an empirical equation fitted to the equilibrium data obtained for temperatures between 5° and 55°C. by Young, Klotz, and Singleterry (57, 61). The equation gives for 25°C.: $\Delta F^0 = 2721$ cal. mole^{-1}, $\Delta H^0 = -5188$ cal. mole^{-1}, and $\Delta C^0_p = -46$ cal. mole^{-1} degree.$^{-1}$

The results of the calculations are compared in figure 8 with the experimental data of Lange, Monheim, and Robinson (28). Their experimental values were

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[6] Existing measurements of the heats of dilution and heat capacities indicate that acids and lithium salts are similar thermochemically (12, 51, 52). However, substitution of sodium sulfate and sodium chloride leads to little change in the results.

obtained from a summation of a series of dilutions, some of which required precision in temperature measurement of 10^{-6}°C. or better. The authors' estimate of the probable error of a single point at the highest dilutions is 40–100 cal. mole.$^{-1}$ At least one of the two points nearest $C = 0$ must be in error by 100 cal. mole^{-1} or more, since it is clear that the original dilution data are internally inconsistent.

The agreement between the theoretical and experimental results over the full range of the data is wholly satisfactory in view of the limited data now available. The theoretical values become more accurate as concentration is reduced, whereas the experimental values become less accurate. Extrapolation based upon the theoretical curve should be very reliable. Since Lange, Monheim, and Robinson extrapolated linearly, all of their results for the integral heats of dilution (table 2 of reference 28) must be reduced by 290 cal. mole.$^{-1}$ Even from the data now available, this correction has been calculated with an uncertainty probably no greater than 10 or possibly 20 cal. mole.$^{-1}$ Better calculations of the curve near $\sqrt{m} = 0.2$ will have to await a complete experimental determination of the heats of dilution of an acid which is nearly completely dissociated, e.g., hydrochloric acid, further knowledge concerning heats of mixing and, especially, better knowledge of the degree of dissociation of the bisulfate ion.

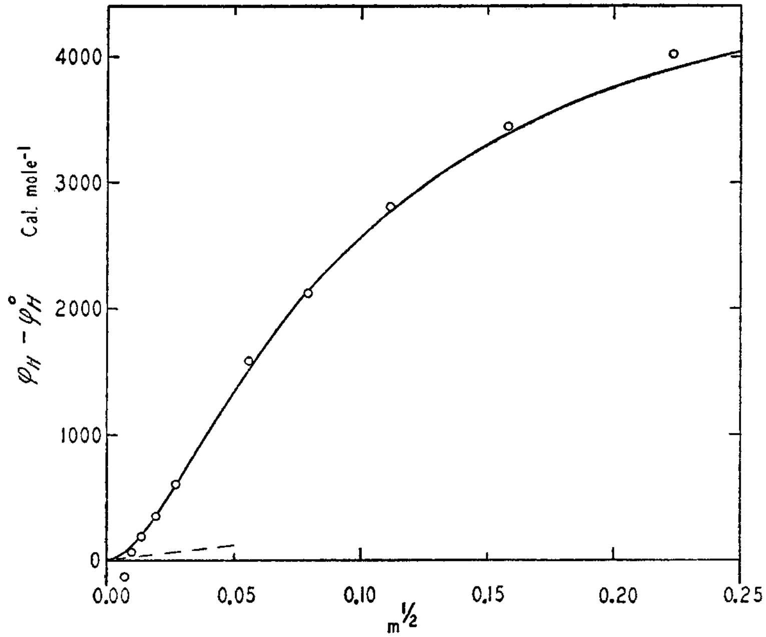

FIG. 8. Relative heat content of sulfuric acid. Curve is calculated. Points are experimental values corrected for error of linear extrapolation. Dashed line shows Debye–Hückel limiting law.

B. Apparent molal volume

The apparent molal volume of sulfuric acid decreases slowly as its concentration is decreased from 3 to about 0.3 molar (see figure 9). It then drops rapidly as the concentration is further decreased. From Klotz and Eckert (23) has come a quantitative explanation of these variations, in terms of the dissociation of the bisulfate ion and the relatively small variations in volume typical of electrolytes which are much more highly dissociated. The latter are ascribed largely to the interionic attractive forces treated by Debye and Hückel (*cf.* Redlich and Bigeleisen (45)). Klotz and Eckert employed the equation:

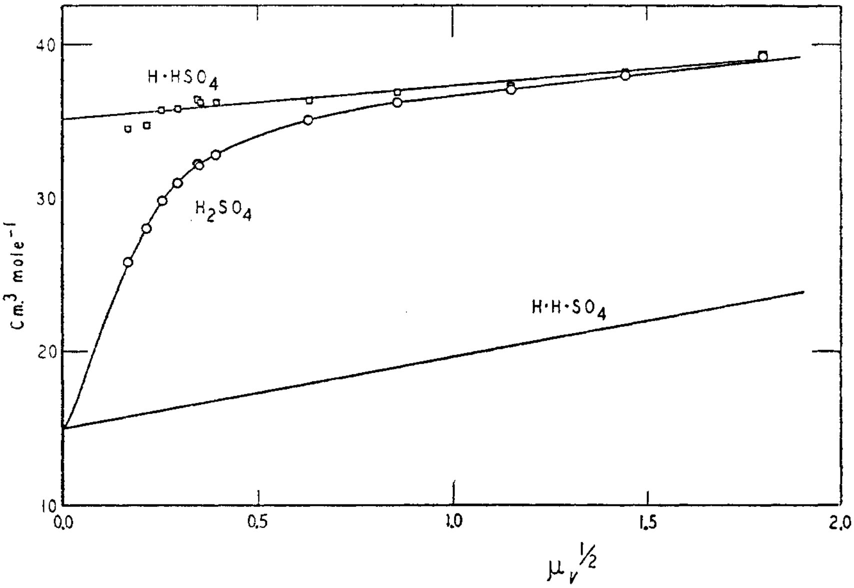

FIG. 9. Apparent molal volumes of $H\cdot HSO_4$, H_2SO_4, and $H\cdot H\cdot SO_4$. Points are experimental.

$$\varphi_V(H_2SO_4) = \alpha\varphi_V(H\cdot H\cdot SO_4) + (1 - \alpha)\varphi_V(H\cdot HSO_4) \qquad (12)$$

and assumed that φ_V of each of the hypothetical solutes is determined (at constant temperature and pressure) by the total ionic strength. They calculated apparent molal volumes for the hypothetical solute $H\cdot H\cdot SO_4$, assuming that apparent molal volumes of ions are additive, and that each φ_V is determined by the total ionic strength.[5] For each of a series of ionic strengths they employed the equation:

$$\varphi_V(H\cdot H\cdot SO_4) = \varphi_V(K_2SO_4) + 2\varphi_V(HCl) - 2\varphi_V(KCl) \qquad (13)$$

The apparent molal volumes were determined from the respective density data for solutions of potassium sulfate, hydrochloric acid, and potassium chloride, all having ionic strengths equal to that of the sulfuric acid.

The lowest curve of figure 9 shows their results. The solid circles of figure 9 represent experimental determinations of the apparent molal volumes of sulfuric acid calculated by Klotz and Eckert from densities which they had determined with a precision of about one in 10^6. The open circles of the figure represent apparent molal volumes of $H \cdot HSO_4$ calculated by means of equation 12 from measured values of φ_V for H_2SO_4, the theoretical curve for $H \cdot H \cdot SO_4$, and the degrees of dissociation of HSO_4^-. The degrees of dissociation they estimated by a method which gave essentially the same results for the apparent molal volume as the upper γ_R line in figure 7. The fact that the curve so obtained for $H \cdot HSO_4$ is nearly linear within the experimental range and has about the slope expected for an acid of 1-1 valence type is evidence for the essential correctness of the procedures used.

Klotz and Eckert completed their beautiful analysis by estimating $\Delta\varphi_V^0$ for the dissociation of HSO_4^- (-20.2 cm.^{3} mole^{-1}) and calculating the portion of the curve for H_2SO_4 between the origin and the first experimental point.

C. Surface tension

Surface tensions of aqueous solutions of most strong electrolytes other than acids are nearly linear functions of concentration (20). In all of the measured surface tension isotherms of sulfuric acid there are prominent maxima. In the isotherm for 0°C. there is also a shallow minimum (see figure 10). The minimum becomes less pronounced as temperature rises and seems to disappear at about 55°C. (20, 34, 50).

Young and Grinstead (60) have recently attempted to determine to what extent varying degrees of dissociation are responsible for these phenomena. Observing that contributions of various ions to the surface tension are approximately additive except when hydrogen ion is in the presence of a second positive ion, they determined surface tension curves for dilute solutions of the hypothetical solute $H \cdot H \cdot SO_4$. The surface tension at any molality m' was taken to be the sum of the surface tension of a sodium sulfate solution of that molality plus the surface tension of a hydrochloric acid solution of twice that molality minus the surface tension of a sodium chloride solution of molality equal to $2\ m'$. The curves so computed are shown as short lines in figure 10. By a somewhat similar procedure curves were also determined for the other hypothetical solute $H \cdot HSO_4$.

The surface tension of sulfuric acid of molality m' was then computed as the sum of the surface tension of $H \cdot H \cdot SO_4$ at a molality $\alpha m'$ and the surface tension of $H \cdot HSO_4$ at a molality $(1 - \alpha)m'$.

Surface tension data for solutions of all electrolytes except hydrochloric acid were taken from the compilation by Young and Harkins in the *International Critical Tables* (20). For hydrochloric acid the tables were not adequate because they do not show temperature variations of $\Delta\gamma$, the difference between the surface tension of a solution and that of pure water. An early attempt to explain the curves of figure 10 met with complete failure because $\Delta\gamma$ of hydrochloric acid was assumed to be nearly independent of temperature, as it is for most strong electrolytes. Hoping to locate the cause of the failure, Young, Runge, and Grinstead (53, 63) made measurements at 0°, 20°, and 40°C. They found the surface tension lowering of dilute hydrochloric acid to vary rapidly with temperature; the lowering is much larger at 0°C. than at 18°C. At 40°C. $\Delta\gamma$ is actually positive for all concentrations between 0 and 8 molal.

The new surface tension data led to very different theoretical calculations. Table 4 contains a comparison of experimental and theoretical points on the 0°C. and 18°C. isotherms. The agreement is nearly as good as might be expected if there were no uncertainty in the degrees of dissociation estimated from a single approximate γ_R curve for both 0°C. and 18°C.

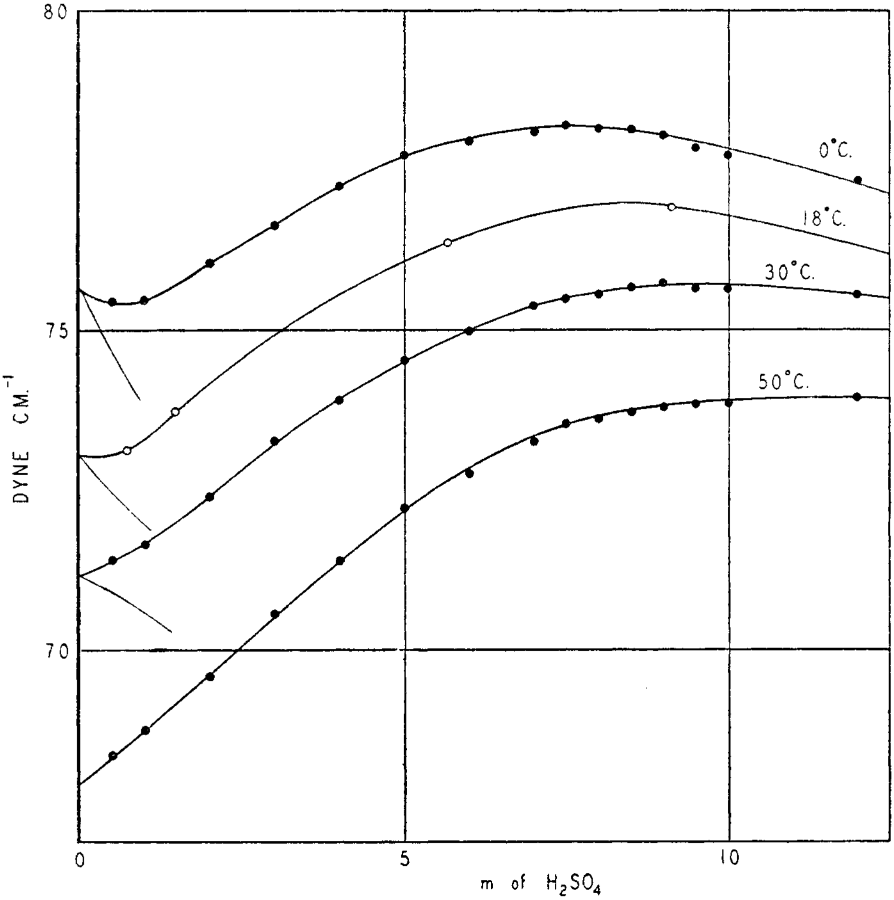

FIG. 10. Surface tension (dynes cm.$^{-1}$) of sulfuric acid solutions at 0°, 18°, 30°, and 50°C. Light lines are theoretical curves for $H\cdot H\cdot SO_4$.

Estimation of the height and position of the maximum surface tension is more difficult. Some of the principles and approximations acceptable when the concentrations are small become unreliable at higher concentrations. Probably the most serious source of error is the neglect, in this simple procedure, of the effects of $\cdot HHSO_4$. According to the calculations made without any allowance for the effects of $\cdot HHSO_4$ the maximum $\Delta\gamma$ should occur in the solution of about the concentration in which the hydrogen-ion and bisulfate-ion concentrations are maximal (65 weight per cent). Actually, $\Delta\gamma$ reaches a maximum of 3.9 dynes cm.$^{-1}$ in a 47 per cent solution.

A rough estimate of the effect of $\cdot HHSO_4$ in the 47 per cent solution may be made. Consider the solution to be one containing the solute ions H^+, HSO_4^-, and SO_4^{--} in a mixed solvent consisting of H_2O and $\cdot HHSO_4$. The mole fraction of $\cdot HHSO_4$ in the hypothetical solvent (separated from the solute ions) would be 0.024. The surface tension of the solvent would probably be less than that of pure water. Linear interpolation on a mole fraction scale between γ of water and γ of pure sulfuric acid leads to a value for γ for the mixture which is 0.5 dyne cm.$^{-1}$ less than that of water. Surface tensions of mixtures are usually considerably lower than linear interpolation would indicate. The correction to be expected, therefore, is larger than 0.5, perhaps as much as twice that. The difference between the experimental maximum $\Delta\gamma$ (3.9), and $\Delta\gamma$ calculated (5.0) for the 47 per cent solution is therefore about what is to be expected.

TABLE 4

Comparison of calculated and experimental points on surface tension isotherms

	0°C.		18°C.	
	Calculated	Observed	Calculated	Observed
m at which $\Delta\gamma = 0$	1.5	1.3	0.04	Small*
m at which $d\gamma/dm = 0$	0.65	0.5–0.7	0.02	Small*
Minimum $\Delta\gamma$	−0.15	−0.21	−0.01	Small*
$\Delta\gamma$ at $m = 0.7$	−0.15	−0.21	−0.25	0.06
$\Delta\gamma$ at $m = 1.5$			0.72	0.67

* Too small to estimate.

The surface tension results constitute a strong argument for the correctness of the picture of sulfuric acid coming from the Raman data. There is additional support for the picture in conductance data. The product of viscosity and specific conductance is greatest in a solution of about the same composition as that in which the hydrogen-ion concentration is largest (25).

D. Apparent molal heat capacity

The equation for the theoretical calculation of the relative apparent molal heat capacity is obtained from equation 11 by differentiation of both sides with respect to temperature. When ΔH of mixing is negligible, the equation is:

$$\begin{aligned}\underset{\mathrm{H_2SO_4}}{\varphi_C - \overset{0}{\varphi_C}} = {} & [\Delta H^0_{\mathrm{Dis}} + \underset{\mathrm{H\cdot H\cdot SO_4}}{(\varphi_H - \overset{0}{\varphi_H})} - \underset{\mathrm{H\cdot HSO_4}}{(\varphi_H - \overset{0}{\varphi_H})}]\left(\frac{\partial\alpha}{\partial T}\right)_m \\ & + (\alpha - 1)\Delta C^0_{\mathrm{Dis}} + \alpha\underset{\mathrm{H\cdot H\cdot SO_4}}{(\varphi_C - \overset{0}{\varphi_C})} + (1 - \alpha)\underset{\mathrm{H\cdot HSO_4}}{(\varphi_C - \overset{0}{\varphi_C})} \qquad (14) \\ & + \alpha\underset{\mathrm{H\cdot H\cdot SO_4}}{\left(\frac{\partial\varphi_H}{\partial\mu}\right)_T\left(\frac{\partial\mu}{\partial T}\right)_m} + (1 - \alpha)\underset{\mathrm{H\cdot HSO_4}}{\left(\frac{\partial\varphi_H}{\partial\mu}\right)_T\left(\frac{\partial\mu}{\partial T}\right)_m}\end{aligned}$$

In equation 14 φ_H and φ_C denote properties of the hypothetical solutes in solutions of ionic strengths equal to the ionic strength of the sulfuric acid solution.

There have been two excellent experimental studies of the apparent molal heat capacities of sulfuric acid: one by Biron (3) in 1899 and a more recent one by Randall and Taylor (38). Their determinations of φ_C are in excellent agreement. $\varphi_C - \varphi_C^0$, the relative apparent molal heat capacity, was determined by Randall and Taylor only. For that purpose they computed the apparent molal heat capacity of infinitely dilute sulfuric acid from available published values of φ_C^0 for hydrochloric acid, sodium sulfate, and sodium chloride. The limiting heat capacities had been determined by linear extrapolation to infinite dilution of measured values of φ_C of the respective electrolytes. This procedure has been shown by Young and Machin (62) to be erroneous. In general, it leads to values of φ_C^0 which are too low.

Data are not now available for a satisfactory demonstration of the use of equation 14. Nevertheless, we have ventured to make a calculation based upon the γ_R curves of figure 7, and the equilibrium constants determined by Young, Klotz, and Singleterry (57, 61). In the absence of any knowledge concerning the variation of γ_R with temperature it was necessary that its temperature coefficient be treated as though it were zero. This approximation is especially unsatisfactory for the calculation of a temperature derivative. Thermal data for the solutions of lithium salts used as analogues of $H \cdot H \cdot SO_4$ and $H \cdot HSO_4$ were also grossly inadequate. When necessary, values of relative apparent molal heat contents and heat capacities were estimated from the tables of properties of similar electrolytes compiled by Gucker and Schminke (12), Young and Seligmann (64), Randall and Rossini (37), and Rossini (51, 52). The result is shown in table 5. The agreement is entirely satisfactory; the discrepancy is no larger than is to be expected as a result of the various approximations. It is not much larger than the uncertainty (due to extrapolation) in the experimental value itself.

TABLE 5

Apparent molal heat capacity of sulfuric acid

C	EXPERIMENTAL		CALCULATED
	φ_C	$\varphi_C - \varphi_C^0$	$\varphi_C - \varphi_C^0$
0.1	9	76	65

The discrepancy in this calculation, like those in others discussed above, points to the need for adequate optical, thermodynamic, and other relevant data. The demand is rather for measurements made over sufficiently wide ranges of temperature, concentration, and pressure than merely for improved accuracy. When the necessary information is available, it should be possible to increase the beauty and precision of calculations such as these and greatly improve our understanding of the behavior of solutions of those interesting electrolytes which are moderately strong but by no means completely dissociated.

We are grateful to Professor G. Herzberg for an inspiring conversation concerning these calculations. Our hearty thanks are also extended to Messrs. L. F. Maranville and H. M. Smith and to Dr. C. R. Singleterry, who have helped with calculations and handling of the data.

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