25° isotherm for hydrogen has been determined. The method employed is believed to be free from the serious errors of other work in this field.

It was found that hydrogen and carbon monoxide were adsorbed to practically the same extent, while the oxygen adsorption was only about half as great. A consideration of the effect of temperature on these adsorptions leads to the conclusion that at somewhat higher temperatures all three gases would be adsorbed in more nearly equal amounts.

Of especial interest is the fact that the results support the hypothesis of unimolecular (or monatomic) adsorbed films.

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THE INTER-IONIC ATTRACTION THEORY OF IONIZED SOLUTES

VI. THE IONIZATION AND IONIZATION CONSTANTS OF MODERATELY IONIZED ACIDS

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Principles of the Method

The theory of inter-ionic attraction developed by Milner and by Debye and Hückel[1] has been tested and found to account satisfactorily, at any rate at low concentration, for the anomalous behavior of salts, acids and bases which may be assumed to be completely ionized. In case of slightly ionized acids or bases, the effect of ion attraction is small on account of the low ion concentration in such solutions. In the case of acids or bases which lie between these two extremes (the so-called half-electrolytes) the effect is large; and it is the purpose of this paper to apply certain principles derived from the theory to the evaluation from conductance data of the true ionization and of the ion activity of such substances.

The usual method of calculating the ionization of acids from the conductance ratio Λ/Λ_0 becomes inexact in case of moderately ionized acids, since according to the inter-ionic attraction theory the mobility of the ions decreases when their concentration increases. The exact mathematical treatment of this effect has been developed by Debye and Hückel, and they have derived an expression for the ratio of the mobility of a given ion in a solution of (small) ionic strength[2] to the mobility of that ion at zero

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[1] (a) Milner, *Phil. Mag.*, **23**, 551 (1912). (b) **25**, 742 (1913). (c) Debye and Hückel, *Physik. Z.*, **24**, 185, 334, 305 (1923). See also (d) Noyes, THIS JOURNAL, **46**, 1080, 1098 (1924); and (e) Hückel, "Zur Theorie der Elektrolyte," *Ergebnisse der exakten Naturwissenschaften*, Julius Springer, Berlin, **1924**, vol. 3, pp. 256–275.

[2] The term ionic strength is here used, as defined by Lewis and Randall [THIS JOURNAL, **43**, 1141 (1921)], to denote one-half of the sum, taken for all the kinds of ions in the solution, of the products of the molal concentration c of each ion by the square of its valence, z, that is, to be equal to $\frac{1}{2}\Sigma(cz^2)$.

concentration, which shows that the fractional decrease in mobility of a given ion at any definite temperature is a function of the ionic strength of the solution. This is the principle that is employed in this article. The exact Debye-Hückel expression, to be sure, is valid only for very small ionic strengths. Moreover, the specific nature of the other ions present in the solution theoretically has an effect even at very small concentrations. Nevertheless, it is to be anticipated that these deviations from the principle will not produce an important effect on the correction on the mobilities, up to moderate concentrations, since the whole correction will be shown to be relatively small, especially when compared with the correction on the ion activities.

On the experimental side, MacInnes[3] has shown, by combining conductance with transference data and assuming complete ionization, that the mobility of certain monatomic univalent ions (H^+, K^+, Cl^-) up to 0.1 *N* is independent of the other ion with which it is associated, provided the latter is also monatomic and univalent. He mentions, without citing data, that this principle is not accurate when applied to nitrates or chlorates. We have made a similar comparative study of ions in solution of unibivalent salts and uni-univalent salts; this shows that the mobilities of a definite ion (for example, K^+) at a given ionic strength differ considerably from each other in solutions of salts (such as KCl and K_2SO_4) of the two valence types. Nevertheless, this principle gives results sufficiently exact for the purpose, especially if the mobilities used are derived from the known conductances of ions that have the same valence and similar molecular complexity as those existing in the solutions to be investigated.

The method here used of applying this ionic-strength principle for evaluating the mobilities of ions and the ionization of moderately ionized acids from conductance measurements is most readily explained by considering the case of a solution containing a single di-ionic acid H^+A^- at concentration c normal. The equivalent conductance Λ of the acid is determined by its ionization γ and by the ion mobilities U_H and U_A, or by the corresponding ion-conductances Λ_H and Λ_A,

$$\Lambda = \gamma\ (U_HF + U_AF) = \gamma\ (\Lambda_H + \Lambda_A)$$

The value of the sum of the ion conductances at a given ionic strength, which in this case is equal to γc, is obtained by the additivity principle from the equivalent conductances of the completely ionized substances H^+Cl^-, Na^+A^- and Na^+Cl^- at that ionic strength.

This method evidently differs from the usual method of evaluating the ionization of an acid by the relation $\gamma = \Lambda/\Lambda_0$ only in the respect that there is substituted for the Λ_0 value a value corrected for the decreased mobilities of the ions. The applications imply also the assumption that the largely

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[3] MacInnes, THIS JOURNAL, 43, 1221, 1223 (1921).

ionized substances HCl, NaCl and NaA are completely ionized up to the moderate ionic strengths involved—an assumption which has been made probable by the recent discussions of the theory.

In calculating the ionization constant of the acid by the mass-action expression the so-determined ion concentrations γc must be corrected for the activation which results from the ion attraction, even at smaller ion concentrations. The expression for the ionization constant K then becomes

$$K = \frac{(\alpha_H \gamma c)\ (\alpha_A \gamma c)}{(1-\gamma)c} = \frac{\alpha_H \alpha_A \gamma^2 c}{1-\gamma} \tag{1}$$

Here α_H and α_A represent the activity coefficients or activations of the two ions at the prevailing ionic strength γc.

The ion-attraction theory requires for very small ionic strengths that the activation α_A of any ion A of valence z_A be given by the following equation,[4] when the ion concentrations are expressed in moles per liter.

$$\log_{10} \alpha_A = -1.283 \times 10^{-6} \frac{z^2{}_A \sqrt{\Sigma(cz^2)}}{(\kappa T)^{1.5}} \tag{2}$$

At higher ionic strengths the size of the ion and nature of the other ions present enter as factors.

This principle, combined with the assumption that at moderate ionic strengths the activations of potassium ion and chloride ion are equal, makes it possible to calculate the separate activation of any ion from the ion-activation products experimentally determined for various salts and acids. This hypothesis was proposed by MacInnes,[5] and employed by Lewis and Randall,[6] in evaluating the activations of the separate ions.

The activations α_H and α_{SO_4} of hydrogen ion and of sulfate ion at various ionic strengths were obtained by applying these principles to the ion-activation products for potassium chloride and hydrochloric acid recently derived by Scatchard[7] and to those for potassium sulfate derived by us from the freezing-point measurements of Hall and Harkins[8] and of Hovorka and Rodebush[9] by the methods[10] of Lewis and Randall and of Scatchard.

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[4] See Noyes, Ref. 1d, p. 1095.

[5] MacInnes, *ibid.*, **41**, 1088 (1919).

[6] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., **1923**, p. 381.

[7] Scatchard, THIS JOURNAL, **47**, 644, 654 (1925).

[8] Hall and Harkins, *ibid.*, **38**, 2674 (1916).

[9] Hovorka and Rodebush, *ibid.*, **47**, 1619 (1925). Rodebush, *ibid.*, **48**, 709 (1926). Our computed values of $(\alpha_K^2\ \alpha_{SO_4})^{\frac{1}{3}}$ agree completely with those recently published by Rodebush, which furnish a striking confirmation of the validity of the limiting form of the Debye-Hückel equation for unibivalent salts.

[10] Values of the quantity j as defined in terms of freezing-point lowering by Lewis and Randall [Ref. 6, Equation 2, p. 342] were obtained by the procedure employed by Scatchard, assuming it to have, in accordance with the Debye-Hückel theory, for a unibivalent salt at 0°, the form $j = 1.30\ c^{\frac{1}{2}} - \beta c$. Here β is a constant for a given salt, which we derived for potassium sulfate (as equal to 2.77) from the value of j correspond-

These activation values are given in Table I. They refer partly to 0° and partly to 25°; but the small change with the temperature is here disregarded.

TABLE I

ACTIVATION OF HYDROGEN AND SULFATE IONS AT VARIOUS IONIC STRENGTHS

Ionic strength	*0.001*	*0.005*	*0.010*	*0.020*	*0.050*	*0.100*	*0.200*
$(\alpha_K\alpha_{Cl})^{\frac{1}{2}} = \alpha_K = \alpha_{Cl}$	0.966	0.927	0.900	0.867	0.813	0.767	0.717
$(\alpha_H\alpha_{Cl})^{\frac{1}{2}}$	.966	.931	.909	.880	.836	.802	.778
$(\alpha_K{}^2\alpha_{SO_4})^{\frac{1}{3}}$	.934	.860	.814	.755	.661	.583	...
α_H	.966	.935	.918	.893	.860	.839	.844
α_{SO_4}	.872	.741	.665	.573	.437	.336	...

For convenience in finding the activations of these ions at other ionic strengths, values of the logarithms of these ion activations were plotted against the square root of the ionic strength.

For finding the activation of the other anions ($H_2PO_4^-$, HSO_3^-, HSO_4^-) of the acids involved in this investigation, values of the ion-activation products are lacking. Therefore, Equation 2, representing the ion-attraction theory at very small ionic strengths, was employed for this purpose in the following form which it assumes for univalent ions in water solutions at 25°.

$$\log_{10} \alpha = -0.357\sqrt{\Sigma(cz^2)} \qquad (3)$$

It is doubtless true that the activation values thus obtained are somewhat in error; but, in view of the fact that the anions of most oxygenated acids (such as NO_3^-) do not deviate greatly from the theory, the error is probably not very large.

Ionization Relations of the First Hydrogen of Phosphoric Acid

The best conductance data available for the calculation of the sum of the equivalent conductance at 18° of H^+ and $H_2PO_4^-$ at different ionic strengths are brought together in Table II.

TABLE II

MOLAL CONDUCTANCES OF THE IONS OF PHOSPHORIC ACID AT 18°

Concn. *c*	NaH_2PO_4	HCl	NaCl	$H^+ + H_2PO_4^-$
0.000	70.0	378.3	108.99	339.3
.001	66.22	375.9	106.49	335.6
.005	65.21	372.6	103.78	334.0
.010	63.86	369.3	101.95	331.2
.020	60.28	365.5	99.62	326.2
.050	57.55	358.4	95.71	320.2
.100	53.95	351.4	92.02	313.3

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ing to the actual freezing-point lowering (0.05005°) at 0.01 molal. Values of the activation product $(\alpha_K^2\,\alpha_{SO_4})^{\frac{1}{3}}$ or mean activation up to 0.01 molal were obtained by substituting this expression for *j* in the general relation between mean activation and molality given by Lewis and Randall (as Equation 3 on p. 343 of Ref. 6). For concentrations above 0.01 molal the mean activations given for potassium sulfate by these authors (in the table on p. 362 of their "Thermodynamics") were changed in the proportion which their value at 0.01 molal bears to our value at 0.01 molal.

The concentrations c in the first column (expressed as formula weights per liter) represent also the ionic strengths, since all of the ions are univalent. The values for the molal conductance of sodium dihydrogen phosphate are those given by Abbott and Bray,[11] as corrected by them for the slight increase in conductance due to the secondary ionization of the $H_2PO_4^-$. Those given for hydrochloric acid and sodium chloride were determined by Goodwin and Haskell,[12] and by Kohlrausch and Maltby,[13] respectively. The values recorded in the last column were obtained by subtracting at each concentration (or ionic strength) the molal conductance of the sodium chloride from the sum of the other two molal conductances.

Table III contains in the second column the observed values of the molal conductance of phosphoric acid (H_3PO_4) at the concentrations c (in formula-weights per liter) at which they were actually measured by Noyes and Eastman.[14] The third column gives the ratios of these values to the extrapolated value 339.3 for zero concentration. The values of λ therefore represent the ionization calculated under the old assumption of constant ion mobilities. The fourth column shows the values ($\Lambda_H + \Lambda_A$) of the sum of the conductances of the H^+ and $H_2PO_4^-$ ions at the ionic strengths (which for this purpose may be taken equal to λc) prevailing in the phosphoric acid solutions. These values were obtained by graphical interpolation from a plot of the data given in the last column of Table II against the cube root of the concentration. In the fifth column are given the ratios which represent the ionization γ calculated by the principle that the ion mobilities are determined solely by the ionic strength. The next two columns contain the activations α_H and α_A of the ions H^+ and $H_2PO_4^-$ derived as described above. The next to the last column contains the values of the ionization constant calculated in the old way under the assumption that the ions have the same mobility and the same activation (unity)

TABLE III

IONIZATION AND IONIZATION CONSTANT OF PHOSPHORIC ACID AT 18°

Concn. c	Λ for H_3PO_4	$\lambda = \Lambda/\Lambda_0$	$\Lambda_H + \Lambda_A$	$\gamma = \Lambda/(\Lambda_H+\Lambda_A)$	α_H	α_A	$\frac{\lambda^2 c}{1-\lambda}$	$\frac{\alpha_H\alpha_A\gamma^2 c}{1-\gamma}$
0.0000	339.3	1.000	339.3	1.000	1.000	1.000	...	...
.0020	283.1	0.834	335.7	0.843	0.958	0.954	0.0084	0.0083
.0125	191.2	.563	332.2	.575	.927	.908	.0091	.0082
.0500	122.7	.362	327.2	.375	.896	.853	.0103	.0086
.1000	96.5	.285	324.1	.298	.879	.818	.0113	.0091

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[11] Abbott and Bray, THIS JOURNAL, **31**, 748 (1909).

[12] Goodwin and Haskell, *Phys. Rev.*, **19**, 369 (1904).

[13] Kohlrausch and Maltby, Landolt-Börnstein-Roth-Scheel "Physikalisch-chemische Tabellen," Julius Springer, Berlin, **1923**, vol. 2, p. 1079.

[14] Noyes and Eastman, *Z. physik. Chem.*, **70**, 353 (1910). No correction was applied for secondary ionization of the acid, since the value of the ionization constant for the second hydrogen shows it to be negligible.

at all concentrations. The last column shows the ionization constant obtained by correcting in the way above described for the change in ionization and in activation with the ionic strength (which is equal to the product γc).

It will be seen from Table III that the corrected ionization γ is larger than the conductance ratio Λ/Λ_0 by 2.1% at 0.0125 *F* and by 4.4% at 0.10 *F*. These differences are not large; but upon the value of the ionization constant they would have a much greater percentage effect. The correction for the activation is much larger than that for the mobility; thus the product $\alpha_H\alpha_A$ has the value 0.842 at 0.0125 *F* and the value 0.719 at 0.100 *F*. It will be seen that the effect on the ionization constant of the two corrections combined is small at the smallest concentration 0.0020 *F*, but becomes large at 0.10 *F*, with the result that the corrected values of the ionization constant shows much less variation with the concentration. Indeed, the corrected values are substantially constant between 0.0020 and 0.0500 *F*, though the ionization of the acid changes from 84.3 to 37.5%. The values show, to be sure, a definite trend at the higher concentrations. This may be due to the fact that the actual activation α_A of $H_2PO_4^-$ (like that of IO_3^-, for example) becomes less than the assumed value calculated by equation (2), which is strictly valid only for very small ionic strengths, or to the fact that the assumption used in calculating α_H is somewhat in error.

The results show that the true ionization constant of the first hydrogen of phosphoric acid has the value of **0.0083** at 18°.

Ionization Relations of the First Hydrogen of Sulfurous Acid

The conductance of sodium hydrosulfite has been measured by Barth,[15] Jellinek,[16] and Lindner.[17] Of these measurements the most careful seem to be those of Lindner; and though they refer to only two concentrations, they have been used here for determining the values of $\Lambda_H + \Lambda_{HSO_3}$. The results are given in Table IV. The values given for hydrochloric acid and sodium chloride were interpolated from the data of Bray and Hunt.[18]

Table IV

Molal Conductances of the Ions of Sulfurous Acid at 25°

Concn.	$NaHSO_3$	HCl	NaCl	$H^+ + HSO_3^-$
0.00	100.3	422.2	125.8	396.7
.00437	96.1	415.8	121.1	390.8
.03760	90.4	401.4	112.9	378.9

That the values are not seriously affected by the secondary ionization of HSO_3^- into H^+ and $SO_3^=$ is shown by the fact that the increase between

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[15] Barth, *Z. physik. Chem.*, **9**, 181 (1892).

[16] Jellinek, *ibid.*, **76**, 340 (1911).

[17] Lindner, *Monatsh.*, **33**, 613 (1912).

[18] Bray and Hunt, This Journal, **33**, 786 (1911).

0.0376 and 0.00437 F is 6.3% for sodium hydrogen sulfite, while it is 7.3% for sodium chloride—thus even less for the former salt.[19] The value (100.3) given in the table for sodium hydrogen sulfite at zero concentration was found by increasing the values at each of the two higher concentrations by the same percentage amount as the value for sodium chloride increases between each of these concentrations and zero concentration, and taking the mean of the two results (100.7 and 99.9).

The conductance of sulfurous acid has been measured by Barth,[15] by Kerp and Baur,[20] and by Lindner.[17] The results of the last two investigations are reproduced in the second column of the upper and lower sections of Table V. That table also presents the calculated values of the ionizations, activations and ionization constants in exactly the same way as those for phosphoric acid in Table III. The values of $\Lambda_H + \Lambda_A$ were obtained by plotting the last two values of this quantity given in Table IV against the cube root of the corresponding concentrations, and interpolating on the straight line connecting the two points for the ionic strengths prevailing in the measured sulfurous acid solutions. The other quantities were computed in the same way as before; thus α_A for the HSO_3^- was again obtained by Equation 3 representing the theory at small concentrations.

TABLE V

IONIZATION AND IONIZATION CONSTANT OF SULFUROUS ACID AT 25°

Concn. c	Λ for H_2SO_3	$\lambda = \Lambda/\Lambda_0$	$\Lambda_H+\Lambda_A$	$\gamma = \Lambda/(\Lambda_H+\Lambda_A)$	α_H	α_A	$\frac{\lambda^2c}{1-\lambda}$	$\frac{\alpha_H\alpha_A\gamma^2c}{1-\gamma}$
0.00	396.7	1.000	396.7	1.000	1.000	1.000	...	...
.00817	267.9	0.675	389.8	0.687	0.933	0.917	0.0115	0.0105
.0536	165.6	.417	382.4	.433	.888	.838	.0160	.0132
.5058	68.4	.172	370.9	.184	.841	.701	.0182	.0124
.01261	244.5	.616	388.3	.630	.924	.902	.0125	.0113
.02498	207.6	.523	385.6	.538	.907	.874	.0143	.0123
.04972	169.5	.427	382.7	.443	.890	.841	.0158	.0131
.1000	134.5	.339	379.4	.354	.872	.803	.0174	.0136
.2583	88.3	.223	375.0	.235	.854	.751	.0165	.0120
.5236	65.3	.164	371.0	.176	.841	.703	.0169	.0116

Here again, it is seen that the corrected ionization values γ are not very much greater than the values λ calculated under the assumption of constant mobility, but that the differences are great enough to have a considerable effect on the ionization constant. The activation correction has, as

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[19] The values that were obtained by Jellinek for the ionization constant of hydrosulfite ion by different methods are so discordant as to have little significance. His final average value 5×10^{-6} is much larger than his own conductance data and those of Lindner indicate. Barth's conductances, to be sure, show a larger increase with decreasing concentration, thus of about 15% between the two concentrations in the table; but it seems almost certain that this early work is unreliable.

[20] Kerp and Baur, *Arb. kaiserl. Gesundheitsamt.*, **26**, 297 (1907); *C. A.*, **4**, **264** (1910).

before, a much larger effect upon the constant, and it causes the values of it to show much smaller variations with the concentration.[21]

As the best value at 25° of the true ionization constant, as derived from these conductance data, **0.012** may be adopted. It may be pointed out that, though the data are not very satisfactory, there is a fair agreement between the two series of constants, derived from the data of Lindner and of Kerp and Baur.

Ionization of Hydrosulfate Ion in Solutions of Sulfuric Acid

It seems of special interest to apply the principles derived from the ion-attraction theory to the ionization relations of sulfuric acid, both because it involves a case where both hydrogens of the acid are ionized, and because better knowledge of the ionization constant of the second hydrogen of this important acid is very desirable.

Noyes and Stewart[22] drew certain conclusions as to its ionization relations by combining transference data and conductance data. Their conclusions were, however, based on the assumption that ion mobilities are independent of ion concentration, that the ions have the activities of perfect solutes, and that the ionization of the first hydrogen of sulfuric acid is equal to that of hydrochloric acid as determined by its conductance ratio.

It is now possible to interpret these data much more accurately with the aid of the new principles. It is still necessary, however, to make some assumption as to the ionization of the first hydrogen of the acid; and the simplest and most probable one is to regard it as completely dissociated up to the moderate concentrations involved. It will be seen later that the results afford justification of this hypothesis. Conductance data alone do not make possible a solution of the problem, as was the case with the acids considered above, since exact knowledge of the equivalent conductance of the HSO_4^- ion is not available. By combining transference numbers with the conductances, however, the conductance of this ion can be eliminated or it can be determined.

Consider a solution containing c formula weights of H_2SO_4 per liter, in which the hydrosulfate ion has an ionization γ. There are then in the solution, per formula weight of acid, $(1+\gamma)$ moles of H^+, $(1-\gamma)$ moles of HSO_4^- and γ moles of $SO_4^=$. If Λ_H, Λ_{HSO_4} and $2\Lambda_{SO_4}$ represent the

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[21] Thus while the values of $\lambda^2c/(1-\lambda)$ increase from 0.011 to 0.016 between 0.0082 and 0.0536 molal, according to Lindner's measurements, those of the corrected ionization constant change only from 0.0105 to 0.0132; or in the case of Kerp and Baur's measurements the increase between 0.013 and 0.100 molal of the uncorrected values is from 0.012 to 0.017, while the increase of the corrected values is only from 0.0113 to 0.0136. At the higher concentrations, 0.26 or 0.51 molal, both series show a decrease of the ionization constant, but the effect of new factors, such as viscosity of the solution, doubtless here comes into play.

[22] Noyes and Stewart, THIS JOURNAL, **32**, 1133 (1910).

molal conductances of these ions at the ionic strength prevailing in the solution, the molal conductance 2Λ of the acid will be given by the equation

$$2\Lambda = (1 + \gamma)\ \Lambda_{H} + (1-\gamma)\ \Lambda_{HSO_4} + \gamma 2\Lambda_{SO_4} \tag{4}$$

The corresponding expression for the hydrogen transference-number τ_H, which is equal to the equivalents of hydrogen migrating into the cathode portion as H^+ minus the moles of HSO_4^- migrating out of it, is as follows

$$\tau_H = \frac{(1 + \gamma)\ \Lambda_H - (1 - \gamma)\ \Lambda_{HSO_4}}{2\Lambda} \tag{5}$$

Solving these two equations, we get

$$\gamma = \frac{\Lambda + \Lambda\tau_H - \Lambda_H}{\Lambda_H + \Lambda_{SO_4}} \quad (6); \qquad \text{and} \qquad \Lambda_{HSO_4} = \frac{\Lambda - \Lambda\tau_H - \gamma\ \Lambda_{SO_4}}{1 - \gamma} \quad (7)$$

In order to solve Equation 6 for the ionization γ of the hydrosulfate ion, values of Λ_H and Λ_{SO_4} at the ionic strength prevailing in the solution must be known. This ionic strength is readily seen to be $c\ (1 + 2\gamma)$. The conductance and transference data available for calculating these ion-conductances at 25° at various ionic strengths are brought together in Table VI. The transference numbers were obtained by graphical interpolation from a plot of the experimental values,[23] or at zero concentration of the values corresponding to the separate ion conductances.[24] The table also contains the values of Λ_{Na} (later required), obtained by subtracting from the equivalent conductance of sodium sulfate the values of Λ_{SO_4}.

TABLE VI

CONDUCTANCES OF HYDROGEN ION, SULFATE ION AND SODIUM ION AT 25°

Formal concn.	Equivalent conductance Λ for			τ_H in HCl	τ_{SO_4} in K_2SO_4	Λ_H in HCl	Λ_{SO_4} in K_2SO_4	Λ_{Na} in Na_2SO_4
	HCl[18]	K_2SO_4[25]	Na_2SO_4[25]					
0.0	422.2	152.6	129.0	0.822	0.514	347	78.4	50.6
.001	420.4	144.8	122.3	.823	.512	346	74.1	48.2
.002	418.6	....	....	.824	..	...	..	..
.0025	...	139.8	117.5	..	.510	344.7	71.3	46.2
.005	415.3	134.4	112.55	.824	.508	342.2	68.3	44.2
.01	411.6	128.1	106.95	.825	.506	339.6	64.8	42.1
.02	406.7	....	....	.826	..	...	..	..
.025	...	118.15	97.9	..	.504	335.9	59.5	38.4
.05	398.4	109.9	90.1	.826	.506	329.1	55.6	75.1
.10	390.4	101.4	81.6	.827	.507	322.9	51.4	30.25
.20	380.2	....	....	.827	..	314.4	..	..

With the aid of interpolated values of Λ_H and Λ_{SO_4} corresponding to those of Table VI, there can be calculated by Equation 6 the ionization of the hydrosulfate ion in any solution of sulfuric acid for which the equivalent conductance Λ and transference number τ_H have been measured.[26]

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[23] Noyes and Falk, THIS JOURNAL, **33**, 1457 (1911).

[24] Noyes and Sherrill, "Chemical Principles," Macmillan Co., N. Y., **1922**, p. 120.

[25] Noyes and Falk, THIS JOURNAL, **34**, 470 (1912).

[26] The values of Λ_H and Λ_{SO_4} prevailing in any sulfuric acid solution are determined by estimating its ionic strength $c(1 + 2\gamma)$ and interpolating from a graph in which the

Table VII contains these values of the ionization γ and the conductance and transference data (as adopted by Noyes and Stewart[27]) from which they are derived. Values of Λ_{HSO_4} calculated by Equation 7 are also given in the table,[28] as they are to be used later.

TABLE VII

IONIZATION AND CONDUCTANCE OF HYDROSULFATE-ION IN SULFURIC ACID SOLUTIONS AT 25°

Formal concn.	Λ for H_2SO_4	T_H for H_2SO_4	Λ_H	Λ_{SO_4}	γ	$\frac{1}{2}\Sigma(cz^2)$	Λ_{HSO_4}
0.00	425.4	0.816	347.0	78.4	1.000	0.0	..
.00025	413.7	.816	346.2	76.3	0.959	.0007	..
.001	390.8	.816	344.0	74.3	.874	.0027	..
.005	336.8	.816	338.9	69.5	.668	.0116	46.8
.00625	327.5	.816	337.9	68.6	.632	.0141	46.0
.0125	299.2	.816	334.4	65.6	.522	.0255	43.5
.0250	273.0	.816	330.0	62.3	.423	.0461	41.4
.0500	251.2	.816	324.4	58.8	.344	.0844	39.7

From these values of the ionization the molal concentrations of the H^+, $SO_4^=$ and HSO_4^- are readily calculated; and by multiplying these by the ion activations the activities (a_H, a_{SO_4}, a_{HSO_4}) of these ions are obtained, which when substituted in the mass-action expression give the true ionization constant. Table VIII contains the results of these calculations.

TABLE VIII

IONIZATION CONSTANT OF HYDROSULFATE ION IN SULFURIC ACID SOLUTIONS AT 25°

Formal concn.	γ	10^3c_H	$10^3c_{SO_4}$	$10^3c_{HSO_4}$	α_H	α_{SO_4}	α_{HSO_4}	$\frac{c_H c_{SO_4}}{c_{HSO_4}}$	$\frac{a_H a_{SO_4}}{a_{HSO_4}}$
0.00025	0.959	0.490	0.240	0.010	0.971	0.888	0.969	0.0118	0.0105
.001	.874	1.874	.874	.126	.949	.798	.941	.0130	.0105
.005	.668	8.340	3.340	1.660	.912	.647	.883	.0168	.0112
.00625	.632	10.20	3.950	2.300	.905	.621	.871	.0175	.0113
.0125	.522	19.03	6.525	5.975	.885	.537	.830	.0208	.0119
.025	.423	35.57	10.57	14.43	.863	.449	.779	.0260	.0130
.050	.344	67.20	17.20	32.80	.844	.355	.714	.0352	.0148

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ion conductances given in Table VI are plotted against the cube roots of the ionic strengths. From these values a more exact value of the ionization (and ionic strength) is obtained by Equation 6. The calculation is then repeated with this value of the ionic strength; this method of approximation being repeated till no further change in the value of γ results. It may be mentioned that the so-calculated value of γ is not very sensitive to errors in the transference number T_H; thus, in the worst case (the 0.05 F solution) an error of 1% in T_H, corresponding to one of about 5% in T_{SO_4}, makes an error of 1.5% in γ.

[27] Noyes and Stewart, Ref. 22, pp. 1139, 1140. It is striking that the transference numbers of sulfuric acid do not change with its concentration; but this may be due to compensation between the varying proportion of HSO_4 in the solution and the changing mobilities of the various ions.

[28] The calculated values of Λ_{HSO_4} at the lower concentrations are omitted, since they are very inaccurate, owing to large multiplication of errors.

It will be seen from Table VIII that, while the mass-action expression in terms of ion concentrations, even though in deriving them correction was made for various ion mobilities, increases 3.0 fold between 0.00025 and 0.05 formal, the expression in terms of activities increases only 1.4 fold. The latter variation is, to be sure, by no means insignificant; but when it is considered that the ionization varies from 0.959 to 0.344 and the ionic strength from about 0.0007 to 0.084, and that the ionic-strength principle used in calculating the conductances and activations is doubtless inexact at the higher ionic strengths, a variation of this magnitude might well have been expected.[29]

As the best value of the true ionization constant (in terms of activities) the number **0.0115** may be adopted, as this was found at concentrations (0.005 − 0.0125 *f*) where the ionization (67–52%) was so great as not to cause large multiplication of errors in the calculations, and where the ionic strength is so small that the ionic-strength principle is still probably fairly exact.

Ionization of Hydrosulfate Ion in Sodium Hydrosulfate Solution

It is possible to calculate the ionization constant of the hydrosulfate ion also from the conductance data for sodium hydrosulfate which were obtained by Stewart.[30] The equivalent conductance Λ of this salt is given in terms of the ionization γ of the hydrosulfate ion and the equivalent conductances of the separate ions at the prevailing ionic strengths by the equation

$$\Lambda = \Lambda_{Na} + (1 - \gamma)\,\Lambda_{HSO_4} + \gamma\,\Lambda_H + 2\gamma\,\Lambda_{SO_4} \qquad (8)$$

This equation is readily solved for the ionization γ. Values for Λ_{Na}, Λ_H and Λ_{SO_4} at various ionic strengths have already been given in Table VI; and from plots of these the required values at intermediate ionic strengths were obtained. To find the needed values of Λ_{HSO_4}, the values

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[29] It may be noted that the mean activity coefficient of sulfuric acid, as defined by Lewis and Randall (Ref. 6, p. 328), in these dilute solutions can be calculated from the data of Table VIII, it being equal to $(\alpha_H{}^2\alpha_{SO_4}(1 + \gamma)^2\gamma/4)^{\frac{1}{3}}$. At the concentration 0.0125 formal, which is favorable for such a calculation, the activity coefficient (0.503) thus found is considerably lower than that (0.584) obtained by interpolation from the values given by Lewis and Randall (Ref. 6, p. 357). The discrepancy is doubtless largely due to the fact that their method of evaluation involved extrapolation of the freezing points of sulfuric acid solutions to zero concentration; for this procedure is inexact in the case of this substance, owing to the presence of HSO_4^- in large and rapidly varying proportions. Our value, though it involved extrapolating the freezing points of potassium sulfate solutions, is to be regarded as the more exact one; and therefore all of the values for the activity coefficient above this concentration tabulated by Lewis and Randall should be corrected by multiplying them by the proportionality factor 503/584 or 0.86. It may also be mentioned that this corresponds to a correction of +265 cal. in the value (—176,500 cal.) given by them for the free energy of formation of $SO_4^=$ at activity 1 molal.

[30] Ref. 22, p. 1156.

given in Table VII were also plotted against the cube root of the corresponding ionic strengths, and the best representative straight line was drawn between the points.

Table IX contains the data and calculated ionization values, displayed in the same form as in Table VII. The ion activations correspond to those given in Table I, or in the case of HSO_4^- ion to those calculated from the theory by Equation 3.

TABLE IX

IONIZATION OF HYDROSULFATE ION IN SODIUM HYDROSULFATE SOLUTIONS AT 25°

Formal concn.	Λ	Λ_H	Λ_{SO_4}	Λ_{Na}	Λ_{HSO_4}	γ	$\frac{1}{2}\Sigma(cz^2)$
0.000391	530.97	345.7	75.7	49.2	49.8	0.966	0.0011
.000781	516.75	344.5	74.6	48.6	49.0	.943	.0022
.001562	494.50	342.7	73.1	47.4	48.0	.905	.0044
.003125	463.30	340.3	70.9	45.9	46.7	.851	.0084
.00625	424.76	337.3	68.0	44.1	45.2	.784	.0160
.0125	381.42	333.0	64.5	41.9	43.3	.707	.0302
.025	337.73	328.2	61.1	39.6	41.1	.628	.0564
.050	297.00	322.0	57.6	36.8	38.3	.556	.1056
.100	261.67	314.3	53.9	33.2	34.8	.500	.2000

A confirmation of the principles involved in this method of calculating the true ionization from conductance data is afforded by a comparison of the value of the transference number of the sulfate constituent in 0.1 formal sodium hydrosulfate solution as experimentally determined by Stewart[31] with that calculated from the data of Table IX by the equation $\Lambda T_{SO_4} = 2\gamma\Lambda_{SO_4} - 2(1-\gamma)\Lambda_{HSO_4}$. These two values of the transference number, 0.346 (measured) and 0.339 (calcd.), are in fair agreement with each other.

Table X contains the values of the ionization constant calculated both from the ion concentrations and from the ion activities (a_H, a_{SO_4}, a_{HSO_4}). The ion activations α_H and α_{SO_4} were interpolated from those given in Table I. The values of α_{HSO_4} were calculated from the ion-attraction theory by Equation 3.

TABLE X

IONIZATION CONSTANT OF HYDROSULFATE ION IN SODIUM HYDROSULFATE SOLUTIONS AT 25°

Formal concn.	γ	$10^3c_{HSO_4}$	10^3c_H or $10^3c_{SO_4}$	α_H	α_{SO_4}	α_{HSO_4}	$\frac{c_H c_{SO_4}}{c_{HSO_4}}$	$\frac{a_H a_{SO_4}}{a_{HSO_4}}$
0.000391	0.966	0.01335	0.3772	0.965	0.863	0.962	0.0107	0.0092
.000781	.943	.0448	0.7364	.953	.814	.946	.0121	.0099
.001562	.905	.1481	1.414	.939	.754	.926	.0135	.0103
.003125	.851	.4641	2.661	.921	.685	.899	.0153	.0107
.00625	.784	1.350	4.900	.901	.604	.863	.0178	.0112
.0125	.707	3.662	8.840	.878	.512	.817	.0213	.0117
.0250	.628	9.300	15.70	.856	.417	.759	.0265	.0125
.0500	.556	22.20	27.80	.838	.319	.685	.0348	.0136

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[31] Ref. 22, p. 1156.

These results show, as in the case of sulfuric acid, that while the mass-action expression in terms of concentrations increases very greatly between 0.0004 and 0.0500 F (thus 225%), yet in terms of activities it shows only a moderate increase (one of 48%). Here again, for the same reasons as in the case of the sulfuric acid results, the value **0.0115** at the intermediate concentrations is to be regarded as the best value of the ionization constant.

It will be noted that this value is identical with that derived from the measurements with sulfuric acid, even though the various ions are present in very different proportions from those prevailing in the sodium hydrosulfate solution. Since un-ionized H_2SO_4, if it existed in the solutions, would be present in much larger proportion in the sulfuric acid solution, this agreement confirms the assumption that the ionization of the first hydrogen of this acid is substantially complete.

The value 0.0115 is much lower than the values 0.02–0.03, found by previous investigators[32] without taking into account the mobility and activity corrections.

Summary

This article describes a method of calculating more accurate values of the ionization of moderately ionized acids than have been heretofore obtained from the ratio Λ/Λ_0 involving the assumption of constant ion-mobilities. Values of the corresponding ionization constants were then calculated in terms of the activities of the ions, whose activations were determined by the usual methods. The principles employed are that the mobility and the activation of a given kind of ion are determined by the ionic strength of the solution, not being dependent on the nature and concentration of the separate ions which give rise to this ionic strength.

The method was applied to calculating the ionizations and ionization constants of the first hydrogens of phosphoric and sulfurous acids, and of the second hydrogen of sulfuric acid, assuming its first hydrogen to be completely dissociated. The relatively small variations of the resulting ionization constants afford justification of the method employed.

Incidentally, the work has led to more reliable values of the ionization constants of these important acids, expressed in terms of activities; namely, to **0.0083** for H_3PO_4 at 18°; **0.012** for H_2SO_3 at 25°; and **0.0115** for HSO_4 at 25°.

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[32] Noyes and Stewart, Ref. 22, p. 1160. Kolthoff, *Rec. trav. chim.*, **43**, 207 (1924). See also Livingston, This Journal, **48**, 52 (1926).