order in peroxide in agreement with the experimental data. The experimentally determined rate constants k_1 and k_{-1} are related to the constants given in eq. 7 and 8 by the equations

$$k_1 = kK_2K_3K_4X^4/K_5K_7^2 \qquad (9)$$

$$k_{-1} = kK_4K_5/K_2K_3X^2 \qquad (10)$$

which show that log k_1 should be proportional to 4 log X and that k_{-1} should be proportional to 2 log $1/X$. The value of $(HSO_4^-)/(H_2SO_4)$, which we designate by X, has been related to the Hammett acidity function, H_0, by the equation[3]

$$H_0 = -8.36 + \log (HSO_4^-)/(H_2SO_4)$$

Values of 4 log X and 2 log $1/X$ as a function of % sulfuric acid were calculated from Brand's data and are shown in Fig. 2. The slopes of these lines are -0.58 and $+0.23$ while the slopes of the log k_1 *vs.* % sulfuric acid and log k_{-1} *vs.* % sulfuric acid are -0.59 and $+0.24$.

The good agreement is further evidence for the proposed mechanism. The nitrosonium ion, NO^+, which is formed in the rate-determining step, is rapidly oxidized to NO_2^+ by a persulfate ion. Since potassium nitrite yields the nitrosonium ion in sulfuric acid, it is just as effective a catalyst as potassium nitrate or nitric acid.

The temperature dependence of k_1 and k_{-1} is shown in Fig. 3, the former being determined in 95.8% sulfuric acid and the latter in 88.9% acid. From the slopes of these lines the activation energy of k_1 is 13.3 kcal. per mole, and of k_{-1} 15.3. Since K_3 and X have negative temperature coefficients and since these appear in the numerator in the equation for k_1 and in the denominator for k_{-1}, the temperature dependence and hence the activation energy of k_1 would be expected to be lower than that of k_{-1}.

The rate-determining step shown above is probably a sequence of steps which may be formulated as

$$NO_2^+ + SO_5NO_2^- \longrightarrow O_2N\text{-}O\text{-}O\text{-}SO_2\text{-}ONO_2$$

$$O_2N\text{-}O\text{-}O\text{-}SO_2\text{-}ONO_2 \longrightarrow NO_3^+ + SO_4^{--} + NO_2^+$$

$$NO_3^+ \longrightarrow NO^+ + O_2$$

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CLARKSON COLLEGE OF TECHNOLOGY]

The Ionization of Sulfuric Acid[1]

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The method of Sherrill and Noyes, based on conductance and transference number, has been used to calculate the ionization of sulfuric acid at 18 and 50° from data in the literature and to extend the results at 25° to higher concentrations. The results have been compared with those obtained by other methods. The effect of the nature of the counterion on the equivalent conductance of sulfate and hydrogen ion has been examined. The equivalent conductance of bisulfate ion has been calculated at 18, 25 and 50°.

The ionization of sulfuric acid has been studied by electromotive force,[2] colorimetry,[3,4] kinetics,[5] Raman spectra[6-8] and a combination of conductance and transference number.[9] Sherrill and Noyes employed transference number as well as conductance data because of the unavailability of the equivalent conductance of the bisulfate ion. Assuming the first hydrogen is completely ionized, they developed the equations

$$\alpha = (\Lambda + \Lambda T - \Lambda_H)/(\Lambda_H + \Lambda_{SO_4}) \qquad (1)$$

$$\Lambda_{HSO_4} = (\Lambda - \Lambda T - \alpha\Lambda_{SO_4})/(1 - \alpha) \qquad (2)$$

where

α fraction of HSO_4^- dissociated

Λ equivalent conductance of H_2SO_4

Λ_H equivalent conductance of H^+ in the H_2SO_4

Λ_{SO_4} equivalent conductance of $SO_4^=$ in the H_2SO_4

Λ_{HSO_4} equivalent conductance of HSO_4^- in the H_2SO_4

T stoichiometric transference number

In solving the above equation, Sherrill and Noyes used values of Λ_H and Λ_{SO_4} obtained from the conductance and transference number of hydrochloric acid and potassium sulfate at the ionic strength prevailing in the sulfuric acid solution under consideration. However, they did recognize that this "ionic strength principle" could not be justified theoretically. Since the ionic strength in the sulfuric acid is given by $m(1 + 2\alpha)$, eq. 1 had to be solved by a series of successive approximations.

The results of Sherrill and Noyes are confined to 25° because of the limited data for T available at that time.[10] In this paper we extend their calculations to 18 and 50° using data which have since appeared in the literature. We have also carried the 25° calculations to higher concentrations.

The stoichiometric transference number, T, which appears in the above equations is related to the individual ionic transference number,[11] t, by

$$T = t_H - t_{HSO_4} \qquad (3)$$

where

$$t_H = c_H\Lambda_H/c\Lambda \qquad (4)$$

$$t_{HSO_4} = c_{HSO_4}\Lambda_{HSO_4}/c\Lambda \qquad (5)$$

and c_H, c_{HSO_4} and c are the normalities of H^+, HSO_4^- and H_2SO_4, respectively. In the Hittorf

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[1] This work has been supported by the Atomic Energy Commission, Contract No. AT (30-1)-1801.

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method T is equal to the number of equivalents of sulfuric acid transferred from anode to cathode region per faraday of electricity passed when electrodes reversible to sulfate ion (*e.g.*, Ag, Ag_2SO_4; Hg, Hg_2SO_4) are used. With the galvanic cell method T is obtained from

$$T = \mathrm{d}E_\mathrm{T}/\mathrm{d}E \qquad (6)$$

E is the electromotive force of the sulfuric acid concentration cell without transference in which the anode is reversible to hydrogen ion and the cathode to sulfate ion. E_T is the electromotive force of the sulfuric acid concentration cell with transference in which both electrodes are reversible to sulfate ion.

Hamer[12] has determined T for sulfuric acid over a wide range of concentration and temperature by the galvanic cell method. He found that T remained constant in the range from 0.05 to 0.2 m and then dropped rapidly with increasing concentration, falling to about 0.5 in concentrated sulfuric acid. Using the Onsager equation, he calculated the variation of t_H with concentration in the infinitely dilute range where the sulfuric acid is completely ionized. Since in this range T would be expected to increase with concentration he suggested that the constancy of T in his dilute solutions was actually a manifestation of a flat maximum and that at concentrations lower than 0.05 m, T would decrease. Hamer's work is discussed by Harned and Owen.[13] Kanning and Waltz[14] extended the work of Hamer to solutions of sulfuric acid in anhydrous methanol at 25°. Ferguson and France[15] had made an earlier study of the same cell as Hamer at 25° for one pair of concentrations.

We have used Hamer's extensive values of T to calculate the dissociation of sulfuric acid at 18 and 50° by the method of Sherrill and Noyes and to extend their results at 25° to higher concentrations. The equivalent conductance of HSO_4^- also has been calculated.

Values of Λ_H were obtained from the equivalent conductance[16,17] and transference number[18,19] of HCl. For Λ_{SO_4} we used the equivalent conductance[20,21] and transference number[22,23] of K_2SO_4. For the equivalent conductance of H_2SO_4 we used the data of Noyes,[20] Kohlrausch,[21] Campbell,[24] and Roughton.[25]

Our results are presented in Tables I, II and III.

The equilibrium quotient K_2' for the second ionization of sulfuric acid extrapolates to the ionization constant K_2, at infinite dilution. The values of the ionization constant at 18 and 50°, as calculated from conductance and transference number data, are reported here for the first time and are compared with the results of other methods in Table IV.

TABLE I

IONIZATION OF H_2SO_4 AND EQUIVALENT CONDUCTANCE OF HSO_4^- AT 18°

Molality of H_2SO_4	Fraction HSO_4^- ionized	Ionic strength	Equilibrium quotient	Quotient of activity coefficients	Equiv. conductance of HSO_4^-
0			0.0124	1	43.6
0.0005	0.936	0.00144	.0141	0.851	
.0010	.888	.00275	.0150	.800	
.0025	.790	.00645	.0168	.714	
.0050	.696	.01196	.0194	.619	40.1
.0100	.600	.0220	.0240	.500	38.7
.0250	.461	.0481	.0312	.385	35.4
.0500	.333	.0835	.0333	.360	32.6
.1000	.317	.1634	.0614	.195	
.2500	.298	.399	.1377	.0871	
.5000	.295	.795	.271	.0443	
1.133	.405	2.05	1.083	.0111	

TABLE II

IONIZATION OF H_2SO_4 AND EQUIVALENT CONDUCTANCE OF HSO_4^- AT 25°

Molality of H_2SO_4	Fraction HSO_4^- ionized	Ionic strength	Equilibrium quotient	Quotient of activity coefficients	Equiv. conductance of HSO_4^-
0			0.0102	1	51.2
0.00025	0.959	0.0007295	.0118	0.864	
.0010	.874	.002648	.0130	.785	
.0050	.667	.01167	.0169	.604	46.8
.0125	.523	.02558	.0209	.488	45.3
.0250	.417	.04568	.0253	.403	39.8
.0500	.336	.08357	.0338	.302	38.7
.1000	.266	.1532	.0459	.222	
.250	.267	.3841	.1185	.0861	
.526	.311	.853	.311	.0328	
.933	.362	1.608	.722	.0141	
1.15	.436	2.16	1.28	.00797	
1.80	.73	4.43	8.31	.00123	

TABLE III

IONIZATION OF H_2SO_4 AND EQUIVALENT CONDUCTANCE OF HSO_4^- AT 50°

Molality of H_2SO_4	Fraction HSO_4^- ionized	Ionic strength	Equilibrium quotient	Quotient of activity coefficients	Equiv. conductance of HSO_4^-
0			0.0053	1	73.3
0.00100	0.764	0.00253	.0057	0.93	
.00500	.493	.00993	.0073	.73	66.5
.00625	.456	.01195	.0076	.70	65.4
.02506	.259	.0376	.0110	.48	59.4
.04016	.214	.0573	.0133	.40	57.5
.05025	.200	.0704	.0151	.35	55.8

Harned and Owen[26] have pointed out the necessity for re-examining the methods of computing ionization constants from electromotive forces for acids as strong as HSO_4^-. They give no weight to

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[12] W. J. Hamer, THIS JOURNAL, **57**, 662 (1935).

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[19] L. G. Longsworth, *ibid.*, **54**, 2741 (1932).

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[26] Ref. 13, p. 430.

TABLE IV

DISSOCIATION CONSTANT OF $HSO_4^- \times 10^2$

Temp., °C.	From conductance and transference no.	From electromotive force Hamer[2b]	Hamer recalcd. by Davies[2b]	Davies[2b]	From spectrophotometry, Klotz[3] and Singleterry[4]
18	1.24	1.30	1.14	1.26	1.26
25	1.02	1.20	1.02	1.03	1.02
50	0.53	0.79	0.69	0.50	0.48

Hamer's electromotive force results, citing instead those of Klotz[3] and Singleterry[4] obtained by a colorimetric method. The temperature dependence of their ionization constants leads to heats of ionization which are in accord with the accepted values, while those of Hamer are in gross disagreement. Klotz and Singleterry report that the error in their results is probably less than 2%. Davies, Jones and Monk[2] have recalculated Hamer's data, introducing correct values of activity coefficients and bringing them into slightly better agreement with the colorimetric work. They have, furthermore, carried out electromotive force measurements in a cell which minimizes the ion association, obtaining results in good agreement with Klotz and Singleterry. The ionization constants calculated from the data of Sherrill and Noyes at 25° and by us at 18 and 50° are also in agreement with the colorimetric work.

Although Sherrill and Noyes recognized that ionic conductivities are not determined by ionic strength, they formally used an ionic strength principle in estimating the equivalent conductance of the sulfate and hydrogen ions in sulfuric acid, and we have followed their heuristic procedure.

We have used the data for potassium sulfate in estimating the equivalent conductance of sulfate ion because they are available over a wide range of conditions. In Tables V and VI there is compiled the equivalent conductance of sulfate ion at several ionic strengths at 18 and 25° as obtained from a number of other salts. For the bi-bivalent salts, where ion association is appreciable, the equivalent conductance of the sulfate ion is calculated from the product of the anion transference number and the equivalent conductance of the salt, divided by the degree of dissociation. The correction for ion association is not so easily made for the uni-bivalent salts but even a rough approximation indicates it is small enough to be neglected. The equivalent conductance of sulfate at 0.1 ionic strength obtained from sodium and potassium sulfate differs from that obtained from thallium sulfate in the direction that would be expected from the greater ion association in the latter.

TABLE V

EQUIVALENT CONDUCTANCE OF SULFATE AT 18° FROM CONDUCTANCE AND TRANSFERENCE NUMBER OF VARIOUS SALTS[27-30]

Ionic strength	Na_2SO_4	K_2SO_4	$CdSO_4$	$CuSO_4$	$MgSO_4$
0.002	63.0	63.4	64.7	66.0	63.5
.010	59.0	59.6	60.0	60.5	58.2
.050	53.8	54.2	54.1	..	..
.100	50.4	51.3	51.8	..	..

TABLE VI

EQUIVALENT CONDUCTANCE OF SULFATE AT 25° FROM CONDUCTANCE AND TRANSFERENCE NUMBER OF VARIOUS SALTS[20-23, 27-30]

Ionic strength	Na_2SO_4	K_2SO_4	Tl_2SO_4	$ZnSO_4$	$CdSO_4$
0.002	76.1	76.0	76.0	76.1	76.0
.010	71.2	71.3	70.0	71.1	70.4
.050	63.4	63.4	59.7	..	63.8
.100	58.9	59.0	53.4	..	61.2

Although the equivalent conductance of the sulfate ion does depend to some extent upon the nature of the cation, the agreement among the results is quite good, especially in view of the uncertainties involved in the ion association of the solutions. Even at 0.1 ionic strength, the fraction ionized would differ by only 1.5% if the equivalent conductance of 53.4 derived from the thallium sulfate data had been used instead of 59.0 derived from the potassium sulfate data.

The fraction ionized α is not very sensitive to the equivalent conductance of sulfate ion since in eq. 1 it is added to the much larger equivalent conductance of the hydrogen ion. This simply transfers the onus of the method to the determination of the equivalent conductance of the hydrogen ion. In Table VII we have compared the values of Λ_H obtained from several monobasic acids at comparable ionic strengths. It is apparent that the anion effect is small. We should like to call attention to the agreement between the hydrochloric and iodic acid results where the available conductance and transference number data are quite accurate. What is especially striking about the agreement is that iodic acid is only partially dissociated so that the equilibrium data have also entered into the calculation much as in the case for the bi-bivalent salts treated above.

TABLE VII

EQUIVALENT CONDUCTANCE OF HYDROGEN ION AT 25° FROM CONDUCTANCE AND TRANSFERENCE NUMBER OF VARIOUS ACIDS

Ionic strength	HCl[16-19]	HNO_3[21,27]	HI[21]	HIO_3[27,31]
0.01	339.9	340	..	339.3
.05	330.9	330	331	330.0
.10	325.5	325	326	...
.20	320.4	..	316	...

The quotient of activity coefficients γ_R is defined by

$$\gamma_R = (\gamma_H)(\gamma_{SO_4^=})/\gamma_{H_2SO_4^-} \qquad (7)$$

and

$$K_2 = K_2'\gamma_R \qquad (8)$$

where K_2 and K_2' are the ionization constant and equilibrium quotient, respectively, and γ_{H^+}, γ_{SO_4} and $\gamma_{HSO_4^-}$ are ionic activity coefficients. Young and Blatz[32] have compared the values of γ_R at 25° obtained in dilute solutions by the conductance and transference number method of Sherrill and Noyes

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and the kinetic method of Bray and Liebhafsky with those obtained in more concentrated solutions by Rao[6] using Raman spectra. Later, Smith[7] and Maranville[8] obtained more accurate Raman spectral data. Since we have extended the values of γ_R at 25° to the concentration range used in the kinetic and Raman spectral studies, it is of interest to compare results again, especially in the overlapping region. Figure 1 is a curve of γ_R at 25° *versus* the square root of the ionic strength. The agreement among the three methods is excellent up to an ionic strength somewhat greater than 1. This agreement is remarkable, especially at the higher ionic strengths. Our only justification for extending the 25° calculations to these high concentrations has been this unexpected agreement among the three methods.

A comment on the work of Bray and Liebhafsky is in order. There was considerable scatter in their results. In plotting a function of γ_R against the square root of the ionic strength, they drew a smooth curve which they presumed was an extrapolation of Sherrill and Noyes conductance and transference number results but which obviously was not the best representation of their own data. Previous workers[7,8,32] have used these smoothed data but we find, despite the scatter, that the actual data of Bray and Liebhafsky give better agreement with both our calculations and the Raman spectral results. In Fig. 1, points representing both their actual and smoothed results are shown.

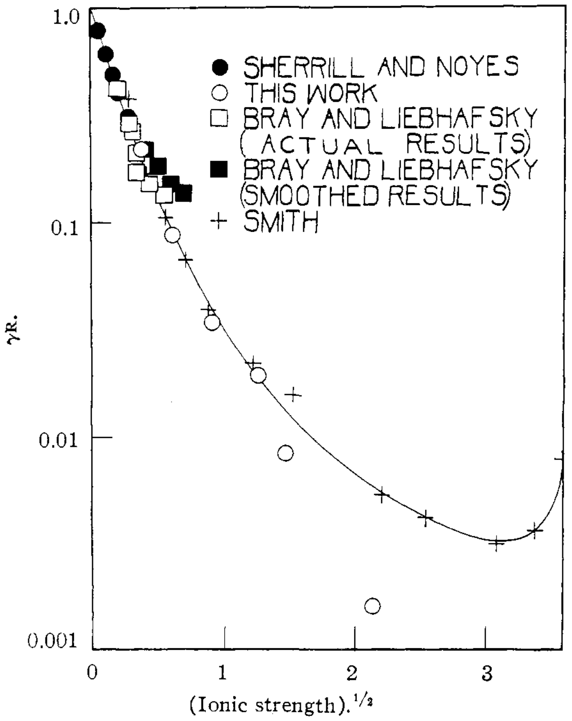

Fig. 1.—Effect of ionic strength on the quotient of activity coefficients, γ_R, of HSO_4^- at 25°.

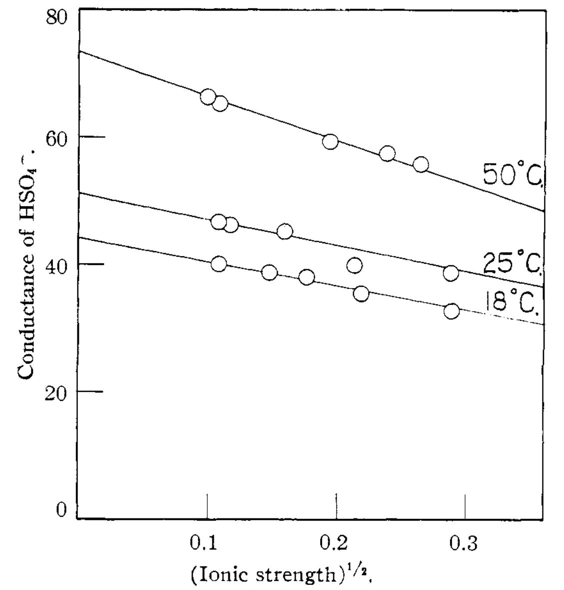

Fig. 2.—Equivalent conductance of HSO_4^-. Circles are computed from conductance and transference number data. Lines are drawn with slope from limiting Onsager law.

The conductance data at 50° do not extend to sufficiently high concentrations to compare γ_R with those from Raman spectra at that temperature.

In Tables I, II and III is also found the equivalent conductance of the bisulfate ion as calculated by eq. 2. In Fig. 2, the equivalent conductance of bisulfate ion is extrapolated to infinite dilution using the limiting Onsager slope for a uni-univalent electrolyte. Since the slope itself is dependent on the intercept, it had to be determined by a series of successive approximations.

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