inherent in the titration method at low *p*H. The limitations of this method have been clearly indicated by Schwarzenbach and Freitag[6] and have been referred to by Holmes and Crimmin[2] in connection with chelates of pyridine carboxylic acids. This source of error, which is greatest in K_1, is augmented at appreciable ionic strengths by uncertainty about the activity coefficient, particularly of the divalent metal ion. The latter difficulty is absent from the present spectrophotometric measurements, where the ionic strength is so low that the activity coefficient can be safely taken as unity. Moreover, the points taken from the work of Suzuki, *et al.*, can be reconciled with our own by using our value of 1.01 for pk_1. Picolinic acid is a fairly strong acid in its first dissociation, so that the term $\gamma k_1 a_H$ is the principal one in the denominator of (2), which is thus fairly sensitive to errors in k_1. If the experimental points of Suzuki, *et al.*, are recalculated using our value of $pk_1 = 1.01$ instead of the earlier spectroscopic value, $pk_1 = 1.60$, then they are moved to the right and do not differ significantly from our *p*H titration figures.

Although the rather large random error appears as a marked degree of scattering in Fig. 5, nevertheless, even after reasonable assumptions have been made about the activity coefficients, the *p*H method still seems to lead to a formation curve significantly lower than that from spectrophotometric measurements, and it becomes necessary to inquire whether some fundamental error in the method of calculation may be responsible for the discrepancy. In the computation of $\bar{n}$ and $[A^-]$ it is assumed that the picolinic acid is either chelated or entirely free from the metal, and, while this is reasonable enough for ligands like ethylenediamine or oxalic acid, it is not quite so obvious for unsymmetrical ligands like the amino acids or picolinic acid. The isoelectric point of picolinic acid is about 3.16, and picolinic acid between *p*H 2 and *p*H 4 is present almost entirely as dipolar ions.[4] While some of these will undergo the normal chelation reaction with metals and contribute normally to the value of $\bar{n}$, others may possibly coördinate with the metal at the carboxylate ion only leaving the pyridinium ion unchanged. An effect of this kind already has been demonstrated[7] for compounds of chromium(III) with alanine, where both chelation and simple carboxylate coördination occur together in the same complex.

In the present case simple coördination would be undetected both in the *p*H method, which is concerned with displacement of the proton of the NH^+ group by a metal ion, and in the spectrophotometric method, since changes in the spectrum depend almost entirely on the state of combination of the nitrogen atom. If such an effect does occur, it will result in the true value of $[A^-]$ being less than the calculated value, so that the calculated experimental points in Fig. 5 will be too far to the left. It is shown easily by an approximate calculation that in this case the error in log $[A^-]$ will be roughly proportional to $m(3 - \bar{n})$, where m is the total nickel concentration. This provides a possible explanation of the results shown in Fig. 5. In the spectrophotometric method, m lay between 5×10^{-6} *M* and 1×10^{-4} *M*, while in our *p*H titrations m was 2.5×10^{-3} *M* throughout. If the effect we have described does occur, its magnitude in our *p*H titrations would be at least 25 times greater than in the spectrophotometric method and might cause the observed displacement of the potentiometric points to the left. The error would be most serious for low values of $\bar{n}$, causing differences particularly in K_1 found by the two methods.

We have therefore not calculated stability constants from the *p*H titrations, since we consider the spectrophotometric method to be superior in this instance, not only because of its lower random error but also because the use of dilute solutions tends to minimize possible systematic errors of the kind we have described.

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[6] G. Schwarzenbach and E. Freitag, *Helv. Chim. Acta*, **34**, 1942 (1951).

[7] R. W. Green and K. P. Ang, THIS JOURNAL, **77**, 5482 (1955).

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[CONTRIBUTION FROM OAK RIDGE NATIONAL LABORATORY OPERATED BY UNION CARBIDE NUCLEAR COMPANY]

The Estimation of Bisulfate Ion Dissociation in Sulfuric Acid–Sodium Sulfate Solutions

BY C. F. BAES, JR.

RECEIVED MAY 6, 1957

From available dissociation and activity coefficient data for pure sulfuric acid solutions, it is pointed out that the product of the ionic activity coefficients ($g^2_{H^+}g_{SO_4^=}$) varies with ionic strength in much the same way as does $(\gamma\pm)^3_{Na_2SO_4}$ for pure sodium sulfate solutions. The assumption that ($g^2_{H^+}g_{SO_4^=}$) shows a similar dependence on ionic strength in sulfuric acid–sodium sulfate solutions is then used to calculate bisulfate ion dissociation in such mixtures. The results are compared with published dissociation measurements in acidic sulfate solutions and with published isopiestic results for sodium bisulfate solutions.

In dealing with the chemistry of acidic sulfate solutions it is often desirable to assign values to the bisulfate ion dissociation quotient

$$Q = [H^+][SO_4^{=}]/[HSO_4^-] \qquad (1)$$

Necessary information concerning the variation of Q as a function of ionic strength and as a function of solution composition, however, is limited. The most reliable and extensive values of Q, primarily for solutions containing sulfuric acid alone, are provided by the Raman measurements of Young and co-workers.[1] In addition, less direct determinations of Q are available as a result of the conduc-

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[1] T. F. Young, *Rec. Chem. Progr.*, **12**, 81 (1951). Private communication from Prof. T. F. Young, L. F. Maranville and H. M. Smith, March, 1956.

tivity calculations of Sherrill and Noyes,[2] the precision colorimetric-indicator measurements of Young, Klotz and Singleterry,[3] the kinetic measurements of Bray and Liebhafsky[4] and the potentiometric measurements of Eichler and Rabideau.[5] The majority of these,[2–4] however, are confined to ionic strengths below *ca.* 0.3 *m*.

The calculations described in the present communication were undertaken in an attempt to estimate the bisulfate ion dissociation quotient for sulfuric acid–sodium sulfate solutions in the vicinity of one molal total solute concentration. The method is based upon the relationship between the dissociation of bisulfate ion and the practical activity coefficient $(\gamma\pm)_{H_2SO_4}$. Thus, while the activity of sulfuric acid $a_{H_2SO_4}$ in such a solution is usually defined in terms of the formal concentrations of hydrogen and sulfate ion, $m_{\Sigma H}$ $(= 2m_{H_2SO_4})$ and $m_{\Sigma SO_4}$

$$a_{H_2SO_4} = m_{\Sigma H}^2 m_{\Sigma SO_4} (\gamma\pm)_{H_2SO_4}^3 \qquad (2)$$

$a_{H_2SO_4}$ may also be defined in terms of the actual concentrations of H^+ and $SO_4^=$

$$a_{H_2SO_4} = [H^+]^2[SO_4^=]g_{H^+}^2 g_{SO_4^=} \qquad (3)$$

Here g_{H^+} and $g_{SO_4^=}$ denote the activity coefficients of the ions in solution. On combining eq. 2 and 3

$$(\gamma\pm)_{H_2SO_4} = \left(\frac{[H^+]^2[SO_4^=]}{m_{\Sigma H}^2 m_{\Sigma SO_4}}\right) g_{H^+}^2 g_{SO_4^=} \qquad (4)$$

it is clear that the ion activity coefficient product $g_{H^+}^2 g_{SO_4^=}$ would equal $(\gamma\pm)_{H_2SO_4}^3$ if sulfuric acid were completely dissociated, since then the ratio in parentheses above would be unity. Because of the incomplete dissociation of bisulfate ion, $[H^+]^2 [SO_4^=]$ is less than $m_{\Sigma H}^2 m_{\Sigma SO_4}$ and so $(\gamma\pm)_{H_2SO_4}^3$ is less than $g_{H^+}^2 g_{SO_4^=}$. Further, it is evident that if $(\gamma\pm)_{H_2SO_4}$ and the dissociation of bisulfate ion are known (*i.e.*, if $[H^+]$ and $[SO_4^=]$ are known) then $g_{H^+}^2 g_{SO_4^=}$ may be evaluated. Conversely, if $(g_{H^+}^2 g_{SO_4^=})$ can be known for a particular solution, then from the corresponding $(\gamma\pm)_{H_2SO_4}$ value the dissociation of bisulfate can be estimated.

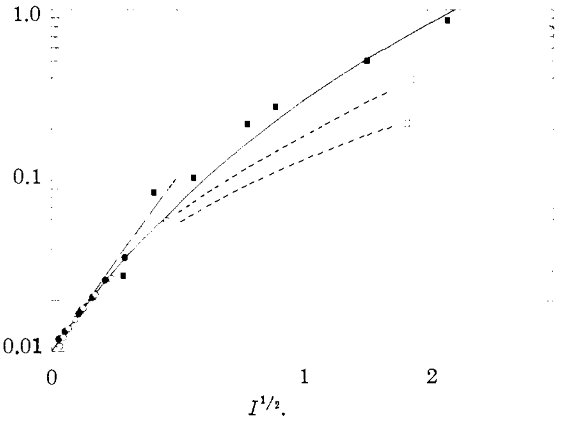

Fig. 1.—The bisulfate ion dissociation quotient Q in acidic sulfate solutions at 25°: ●, H_2SO_4 solutions; ○, $NaHSO_4$ solutions (Sherrill and Noyes[2]); ■, H_2SO_4 solutions; □, NH_4HSO_4 solutions (Young, *et al.*[1]). The solid curve is calculated from eq. 8. The dashed curves represent the present calculations (I) for $NaHSO_4$ and (II) for Na_2SO_4 solutions. The dashed line shows the Debye–Hückel limiting slope.

The procedure in the present calculations will be first to evaluate $(g_{H^+}^2 g_{SO_4^=})$ for solutions containing sulfuric acid alone (hereinafter referred to as pure sulfuric acid solutions) using experimental (smoothed) Q values provided by the Raman data.[1] The resulting values of $(g_{H^+}^2 g_{SO_4^=})$ are found to vary with ionic strength in much the same way as does $(\gamma\pm)_{Na_2SO_4}^3$ for pure sodium sulfate solutions. The assumption that $(g_{H^+}^2 g_{SO_4^=})$ shows a similar dependence on ionic strength in sulfuric acid–sodium sulfate solutions is then used, along with $(\gamma\pm)_{H_2SO_4}$ values obtained from published e.m.f. data, to calculate bisulfate ion dissociation in such mixtures. Assuming H^+, HSO_4^-, $SO_4^=$ and Na^+ to be the only ions present,[6] the ionic strength I is given by

$$I = 3m_{\Sigma SO_4} - 2[HSO_4^-] \qquad (5)$$

which on combination with the material balance expressions $m_{\Sigma H} = 2m_{H_2SO_4} = [H^+] + [HSO_4^-]$ and $m_{\Sigma SO_4} = [SO_4^-] + [HSO_4^-]$ gives

$$[H^+] = (I - 3m_{\Sigma SO_4} + 4m_{H_2SO_4})/2 \qquad (6)$$

$$[SO_4^=] = (I - m_{\Sigma SO_4})/2 \qquad (7)$$

Substitution of these last two expressions into eq. 4 yields a relation in which I and $(g_{H^+}^2 g_{SO_4^=}]$ are the only unknown quantities (*cf.* eq. 11 below) so that with the assumed additional relationship between I and $(g_{H^+}^2 g_{SO_4^=})$ it is possible to determine both quantities for a given solution mixture. Once I is known, $[HSO_4^-]$, $[H^+]$ and $[SO_4^=]$ are known from eq. 5, 6 and 7, and hence Q by eq. 1.

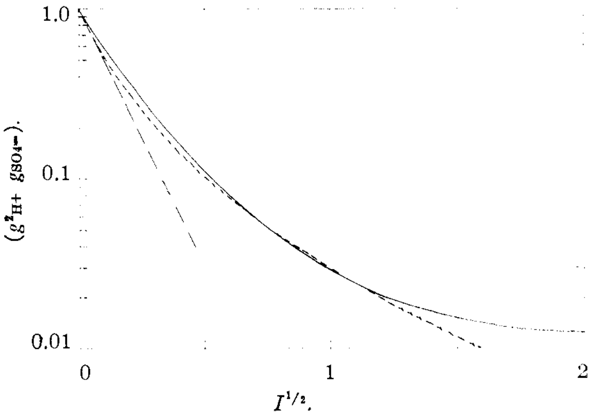

Fig. 2.—The calculated variation of the ion activity coefficient product $(g^2_{H^+} g_{SO_4^=})$ with ionic strength in pure H_2SO_4 solutions at 25°. The dashed curve represents the corresponding plot of $(\gamma\pm)^3_{Na_2SO_4}$ for pure Na_2SO_4 solutions,[10,11] The dashed line shows the Debye-Hückel limiting slope.

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(2) M. S. Sherrill and A. A. Noyes, This Journal, **48**, 1861 (1926).

(3) T. F. Young, I. M. Klotz and C. R. Singleterry, described by R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Academic Press, Inc., New York, N. Y., 1955, pp. 374–376.

(4) W. C. Bray and H. A. Liebhafsky, This Journal, **57**, 51 (1935).

(5) E. Eichler and S. Rabideau, *ibid.*, **77**, 5501 (1955).

(6) On the basis of the Raman measurements of Young, *et al.*,[1] no appreciable amounts of undissociated sulfuric acid are present below *ca.* 11 *M*. Similarly their investigations showed an internal consistency among the integrated Raman intensities of sulfate and bisulfate lines for sulfuric acid and the sulfate lines for sodium sulfate solutions which strongly indicates that sodium sulfate is completely dissociated.

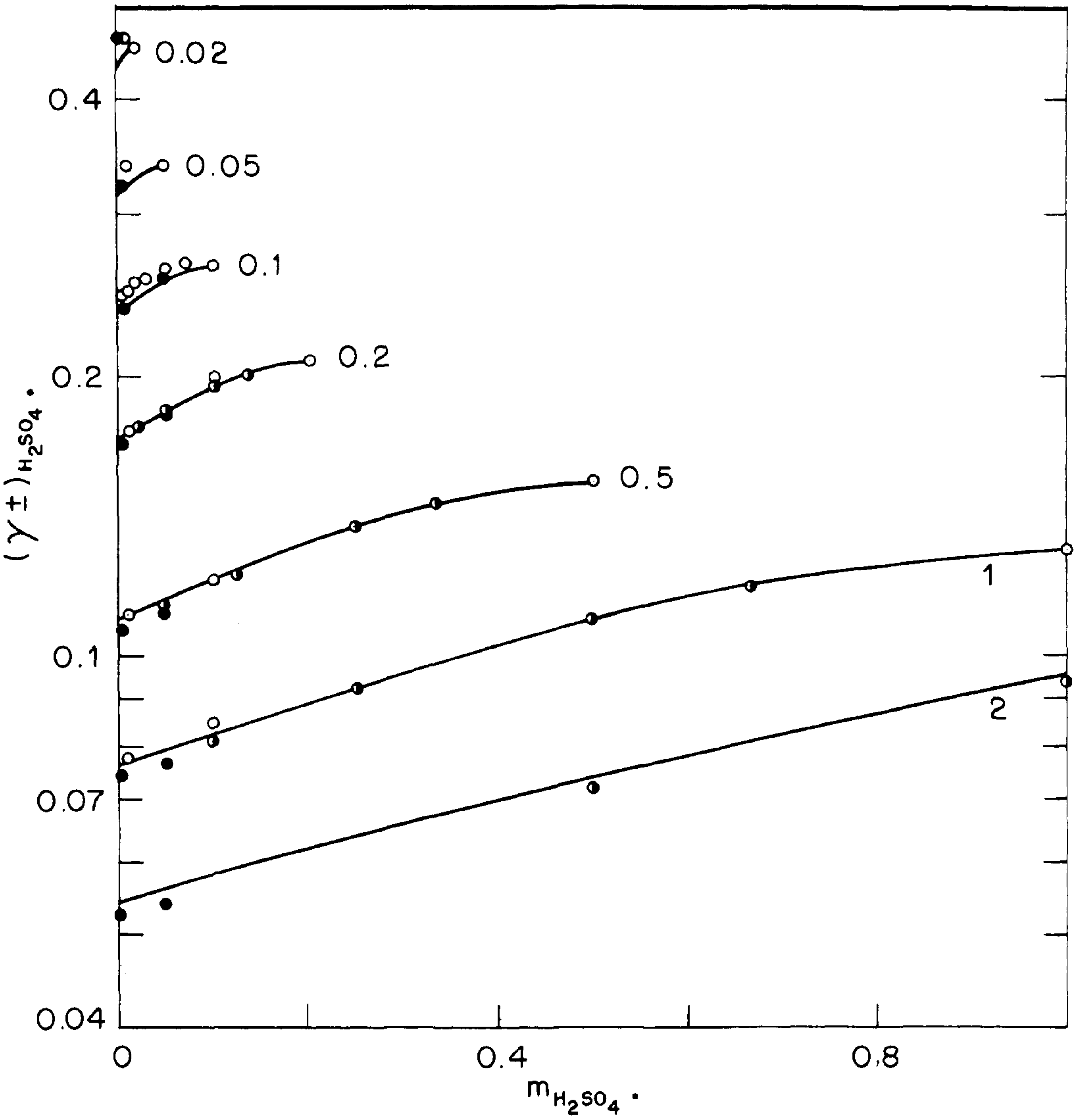

Fig. 3.—The practical activity coefficient, $(\gamma\pm)_{H_2SO_4}$ in H_2SO_4-Na_2SO_4 solutions at 25° from e.m.f. measurements: O, Harned and Sturgis[14]; ●, Åkerlöf[15]; ◑, Randall and Langford.[16] The numbers indicate the total sulfate molality for each series of points. The curves are calculated from eq. 10. Points shown for pure sulfuric acid solutions are those given by Harned and Hamer.[7]

Calculations

Bisulfate ion dissociation quotients in pure sulfuric acid solutions (from the results of Young, *et al.*,[1] and Sherrill and Noyes[2]) are plotted *vs.* $I^{1/2}$ in Fig. 1. Since Sherrill and Noyes were forced to make approximations in their conductivity calculations and since the comparable Raman results were at solution concentrations near the lower limit of that method, the agreement between the two sets of data is excellent, as Young has pointed out.[1] The solid curve drawn through the points was calculated from the equation

$$\log Q = \log 0.0102 + \frac{2.036 I^{1/2}}{1 + 0.4 I^{1/2}} \qquad (8)$$

The indicated infinite dilution value is in good agreement with Young, Klotz and Singleterry's[3] value of 0.01015 *M* for the bisulfate ion dissociation constant.

Using the experimental (smoothed) values of Q provided by eq. 8, along with $(\gamma\pm)_{H_2SO_4}$ values for pure sulfuric acid,[7,8] the ion activity coefficient product ($g_{H^+}{}^2 g_{SO_4^-}$) was calculated from eq. 4.[9]

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[7] H. S. Harned and W. J. Hamer, THIS JOURNAL, 57, 27 (1935).

[8] R. A. Robinson and E. H. Stokes, "Electrolyte Solutions," Academic Press, Inc., New York, N. Y., 1955, p. 462.

[9] The procedure involved first the evaluation of $m_{H_2SO_4}$ from pairs of Q and I values given by eq. 8, using the following relation (obtained by combination of eq. 1, 5, 6 and 7)

$$m_{H_2SO_4} = -3Q + \sqrt{9Q^2 + I(2Q + I)}$$

The concentrations $[H^+]$ and $[SO_4^=]$ were then obtained from equations 6 and 7.

The results are plotted in Fig. 2. The dashed curve is a similar plot of $(\gamma\pm)_{Na_2SO_4}{}^3$ for pure sodium sulfate solutions.[10,11] It is seen that the two curves are nearly superimposed in the range $I = 0.25 - 1.5\ M$.[12]

This similarity between the $(g_{H^+}{}^2g_{SO_4^-})$ and the $(\gamma\pm)_{Na_2SO_4}{}^3$ curves for the unmixed electrolytes suggests the following assumption. The ion activity coefficient product $(g_{H^+}{}^2g_{SO_4^-})$ for all sulfuric acid–sodium sulfate solutions of the same ionic strength is constant and equal to $(\gamma\pm)_{Na_2SO_4}{}^3$ (*i.e.*, $g_{Na^+}{}^2g_{SO_4^-}$) for a pure sodium sulfate solution of that ionic strength. This assumption, restricted to the range $I = 0.25–1.5\ m$, in which the curves are in closest agreement, is analogous to the expected behavior for mixtures of completely dissociated 1-1 electrolytes, each of which exhibits the same activity coefficient behavior in unmixed solutions.[13]

In order to proceed with the calculation of bisulfate ion dissociation in sulfuric acid–sodium sulfate solutions, using this assumption as a means of evaluating $(g_{H^+}{}^2g_{SO_4^-})$, it was necessary first to collect the available information on sulfuric acid activity coefficients in such mixtures. E.m.f. measurements of the cell

$$\text{Pt–H}_2\,|\text{H}_2\text{SO}_4(m),\ \text{Na}_2\text{SO}_4(m')\,|\text{Hg}_2\text{SO}_4\text{–Hg}$$

have been published by Harned and Sturgis,[14] Åkerlöf[15] and Randall and Langford.[16] From their results, the $(\gamma\pm)_{H_2SO_4}$ values plotted in Fig. 3 have been obtained by means of the equation

$$\log\,(\gamma\pm)_{H_2SO_4} = \frac{E^0 - E}{0.088725} - \frac{1}{3}\log\,(4m_{H_2SO_4}{}^2\,m_{\Sigma SO_4}) \quad (9)$$

in which $E^0 = 0.61515$ v.[7,17]

The curves drawn through the points in Fig. 3 were used for the present calculations. They result from the single empirical equation

$$\log\,(\gamma\pm)_{H_2SO_4(x)} = \log\,(\gamma\pm)_{H_2SO_4(c)} - \left[0.2305 - 0.3355\left(\frac{x}{c}\right) + 0.1050\left(\frac{x}{c}\right)^3\right]c^{0.6233} \quad (10)$$

The subscripts (x) and (c) denote activity coefficients in xm sulfuric acid–$(c - x)\ m$ sodium sulfate and in pure cm sulfuric acid,[7] respectively. Since the results of Åkerlöf led to consistently low activity coefficients compared to those calculated from the data of Harned and Sturgis and Randall and Langford, they were given less weight in the determination of the numerical constants.[18]

The method used to calculate Q for sulfuric acid–sodium sulfate solutions can best be illustrated by placing eq. 4 in the form (by combination with eq. 6 and 7)

$$(\gamma\pm)_{H_2SO_4}{}^3 = \frac{(I - 3m_{\Sigma SO_4} + 4m_{H_2SO_4})^2\,(I - m_{\Sigma SO_4})}{32m_{H_2SO_4}{}^2m_{\Sigma SO_4}}\,g_{H^+}{}^2g_{SO_4^-} \quad (11)$$

For a given mixture, successive pairs of I and $(g_{H^+}{}^2g_{SO_4^-})$ values (read from the $(\gamma\pm)_{NaSO_4}{}^3$ curve in Fig. 3) were chosen until the right side of equation 11 was equal to the corresponding experimental (smoothed) value of $(\gamma\pm)_{H_2SO_4}$. Three successive approximations usually were sufficient. The resulting ionic strength along with the given composition of the solution gave $[HSO_4^-]$, $[H^+]$ and $[SO_4^=]$, (eq. 5, 6 and 7) and therefore Q.

For all but three of the calculations (*cf.* footnote *a*, Table I), the ionic strengths fell in the range $I = 0.16$ to $1.8\ m$. Near these limits the deviation of $(g_{H^+}{}^2g_{SO_4^-})$ for pure sulfuric acid from $(\gamma\pm)_{Na_2SO_4}{}^3$ for pure sodium sulfate solutions increases to *ca.* 12% (Fig. 2). Taking this as the maximum deviation of the assumed values of $(g_{H^+}{}^2g_{SO_4^-})$ from the correct values for the mixed solutions, the expected uncertainty in the calculated Q values is *ca.* ± 12%.

Results and Discussion

Calculated bisulfate ion dissociation quotients are summarized in Table I and the corresponding ratios $[HSO_4^-]/m_{\Sigma SO_4}$ in Table II. These results exhibit several interesting features: (1) at constant total sulfate concentration of 0.1, 0.2 and 0.5 m, Q is nearly constant as the composition is changed, even though the accompanying change in ionic strength is considerable; (2) Q changes by as much as a factor of 2.8 with composition at constant ionic strength; (3) plots of log Q *vs.* $m_{H_2SO_4}/m_{\Sigma SO_4}$ at constant I are approximately linear; (4) the ratio $[HSO_4^-]/m_{\Sigma SO_4}$ at a given value of $m_{H_2SO_4}/m_{\Sigma SO_4}$ remains approximately constant as the total sulfate concentration is changed.

The agreement between the calculations for pure sulfuric acid solutions and the observed (smoothed) values of Q and $[HSO_4^-]/m_{\Sigma SO_4}$ (given by eq. 8 and shown in italics in Table I and II) is probably within the limits of uncertainty of the Raman measurements of Young, *et al.*[1] That the calculations for sulfuric acid–sodium sulfate solutions are at least approximately correct is indicated by the com-

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[10] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950, p. 415.

[11] R. A. Robinson and R. H. Stokes, "Electrolytic Solutions," Academic Press, Inc., New York, N. Y., 1955, p. 486.

[12] The deviation shown by the calculated $(g_{H^+}{}^2g_{SO_4^=})$ curve below $I = 0.25$ is somewhat anomalous since the expected Debye–Hückel limiting slope is not approached. In order to superimpose $(g_{H^+}{}^2g_{SO_4^=})$ values on the $(\gamma\ \pm)_{Na_2SO_4}{}^3$ curve in this range, it is necessary to assume Q values as much as 30% higher than those of Sherrill and Noyes[2] or else assume $(\gamma\ \pm)_{H_2SO_4}$ values which are as much as 6% lower than those given by Harned and Hamer.[7]

[13] Referring to the discussion of mixtures of electrolytes by H. S. Harned and B. B. Owen (ref. 12, pp. 461–466), this condition is stated in their notation as $\gamma_{1(0)} = \gamma_{2(0)}$. This corresponds to case (b), (with $B_{12} = 0$) with the result that the activity coefficients of each electrolyte at infinite dilution in the presence of the other (at the same I) are equal; *i.e.*, $\gamma_{0(1)} = \gamma_{0(2)}$. Further, it appears usually true that if $\gamma_{0(1)} > \gamma_{2(0)}$ then $\gamma_{(0)2} < \gamma_{1(0)}$, *i.e.*, that the slopes α_{12} and α_{21} have opposite signs. Assuming that this generality applies here, then the slopes are both zero and $\gamma_1(0)$, $\gamma_{2(0)}$, $\gamma_{0(1)}$, $\gamma_{0(2)}$ and hence also γ_1 and γ_2 are all equal at a given ionic strength.

[14] H. S. Harned and R. D. Sturgis, This Journal, **47**, 945 (1925).

[15] B. Åkerlöf, *ibid.*, **48**, 1160 (1926).

[16] M. Randall and C. T. Langford, *ibid.*, **49**, 1445 (1927).

[17] The results of Åkerlöf, given originally in molarities, were converted to molalities using available density data. In several cases it was necessary to interpolate the results of Harned and Sturgis and Åkerlöf over a short range in total sulfate concentration for the purpose of this plot.

[18] For $m_{\Sigma SO_4} > 0.1\ m$, $(\gamma\pm)_{H_2SO_4}$ values given by this equation agree with those calculated from the results of Harned and Sturgis and Randall and Langford with an average deviation of 0.8% (0.3 mv. in E). Only two values exhibit a deviation greater than 2%. Harned and Hamer have pointed out that the mercurous sulfate electrode becomes unreliable below 0.05 m in pure sulfuric acid solutions because of the appreciable solubility of mercurous sufate. This should produce positive errors in the activity coefficients. Accordingly, the increasing deviation shown by the experimental $(\gamma\pm)_{H_2SO_4}$ values at $m_{\Sigma SO_4} = 0.1$, 0.05 and 0.02 m may result in part from this effect.

TABLE I

CALCULATED BISULFATE ION DISSOCIATION QUOTIENTS IN H_2SO_4–Na_2SO_4 SOLUTIONS AT 25°

$m_{H_2SO_4}/m_{\Sigma SO_4}$	$m_{\Sigma SO_4}$ 0.1	0.2	0.5	1	I 0.4	0.7	1	1.5
0	0.061	0.096	0.178	(0.31)[a]	0.072	0.102	0.131	0.178
.25	.057	.089	.167	(.32)[a]	.079	.117	.150	.207
.50	.056	.085	.172	(.37)[a]	.086	.136	.182	.281
.75	.056	.088	.183	.47	.103	.162	.229	.39
1	.059	.091	.196	.54	.116	.185	.283	.50
1	*.051*[b]	*.084*[b]	*.208*[b]	*.51*[b]	*.108*[b]	*.193*[b]	*.290*[b]	*.48*[b]

[a] The calculated ionic strengths for these mixtures at $m_{\Sigma SO_4} = 1$ are 1.90, 2.33 and 3.00 m at $m_{H_2SO_4}/m_{\Sigma SO_4} = 0.5, 0.25$ and 0, respectively. Since they are above the range specified ($I = 0.16$–$1.8\ m$), the resulting Q and $[HSO_4^-]/m_{\Sigma SO_4}$ values are considered increasingly uncertain. [b] These values are given by cq. 8.

TABLE II

CALCULATED VALUES OF THE RATIO $[HSO_4^-]/m_{\Sigma SO_4}$ IN H_2SO_4–Na_2SO_4 SOLUTIONS AT 25°

$m_{H_2SO_4}/m_{\Sigma SO_4}$	$m_{\Sigma SO_4}$ 0.1	0.2	0.5	1	I 0.4	0.7	1	1.5
0.25	0.28	0.30	0.33	(0.34)[a]	0.30	0.32	0.33	0.34
.50	.48	.53	.56	(.55)[a]	.53	.55	.56	.56
.75	.61	.66	.69	(.65)[a]	.66	.68	.69	.66
1	.69	.74	.74	.70	.74	.76	.75	.71
1	*.72*[b]	*.75*[b]	*.75*[b]	*.72*[b]	*.75*[b]	*.75*[b]	*.74*[b]	*.72*[b]

[a,b] *Cf.* footnotes of Table I.

parisons shown in Fig. 1. It is seen that the present Q values for $m_{H_2SO_4}/m_{\Sigma SO_4} = 0.5$ (*i.e.*, sodium bisulfate solutions) are in good agreement with those determined by Young, *et al.*, for ammonium bisulfate solutions.[1,19] The Q values found by Sherrill and Noyes[2] for sodium bisulfate solutions (at lower ionic strength) similarly are lower than the pure acid values. Further, it is of interest to compare the present values at $I = 1\ m$ with those of Eichler and Rabideau[5] for perchloric acid solutions (containing relatively small amounts of sodium sulfate) at the same ionic strength: $Q = 0.13$ in Na_2SO_4, 0.27 in H_2SO_4; $Q = 0.095$ in $NaClO_4$ (0.01 M $HClO_4$), 0.30 in $HClO_4$. It is seen that both in sulfate and perchlorate solutions, the bisulfate dissociation quotient increases with increasing acidity to approximately the same extent.

Raman measurements on sulfuric acid–sodium sulfate solutions, which when completed will provide probably the best test of the present calculations, are in process at Young's laboratory. The preliminary measurements appear in satisfactory agreement with the calculations.[20]

Stokes[21] has published isopiestic measurements on sodium bisulfate solutions but did not attempt to calculate from them the practical activity coefficient $(\gamma\pm)_{NaHSO_4}$, owing to uncertainties in the extrapolation of the data to infinite dilution. The present calculations may be compared usefully with these measurements in the following manner: In general

$$(\gamma\pm)_{NaHSO_4} = \sqrt{(\gamma\pm)_{H_2SO_4}(\gamma\pm)_{Na_2SO_4}} \qquad (12)$$

Considering only pure sodium bisulfate solutions (*i.e.*, in which $m_{H_2SO_4}/m_{\Sigma SO_4} = 0.5$), eq. 11 gives

$$(\gamma\pm)_{H_2SO_4^-} = ([H^+]/m_{\Sigma SO_4})(g_{H^+}{}^2 g_{SO_4^-})^{1/3} \qquad (13)$$

By equations analogous to eq. 2, 3, 4 and 11, it may also be shown that

$$(\gamma\pm)_{Na_2SO_4} = ([H^+]/m_{\Sigma SO_4})^{1/3}(g_{Na^+}{}^2 g_{SO_4^-})^{1/3} \qquad (14)$$

At this point let it be assumed that, as in the case of $(g_{H^+}{}^2 g_{SO_4^-})$, the product $(g_{Na^+}{}^2 g_{SO_4^-})$ for sulfuric acid–sodium sulfate solutions at constant I is constant and equal to $(\gamma\pm)_{Na_2SO_4}{}^3$ in pure sodium sulfate solutions; then $(g_{Na^+}{}^2 g_{SO_4^-}) = (g_{H^+}{}^2 g_{SO_4^-})$. This condition gives on combination of eq. 12, 13 and 14

$$(\gamma\pm)_{NaHSO_4} = (m_{\Sigma SO_4}/[H^+])^{1/3}(\gamma\pm)_{H_2SO_4} \qquad (15)$$

Table III presents a comparison of $(\gamma\pm)_{NaHSO_4}$ values calculated by this last equation with a series of values derived directly from Stokes' isopiestic measurements upon choosing $(\gamma\pm)_{NaHSO_4} = 0.3087$ at 0.1 m.[22] The agreement between the two sets of activity coefficients is satisfactory.

TABLE III

THE ACTIVITY COEFFICIENT OF SODIUM BISULFATE AT 25°

m	$(\gamma\pm)_{NaHSO_4}$ from eq. 15	$(\gamma\pm)_{NaHSO_4}$ from Stokes' isopiestic results[21,22]
0.1	0.316	(0.3087)
.2	.251	0.250
.5	.182	.1842
1	.142	.1444

Summing up, it has been found that for pure sulfuric acid solutions in the range $I = 0.25$–$1.5\ m$, the ion activity coefficient product $(g_{H^+}{}^2 g_{SO_4^-})$ varies with ionic strength in nearly the same way

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[19] Since the activity coefficient curves for ammonium and for potassium sulfate solutions up to 1 m are quite similar to that of sodium sulfate, it is expected that the dissociation behavior of sulfuric acid in the presence of each salt will be similar in this range. The present treatment was not applied to ammonium sulfate—sulfuric acid and potassium sulfate—sulfuric acid solutions owing to the lack of sufficiently extensive data on $(\gamma\pm)_{H_2SO_4}$ in such solutions.

[20] At the generous invitation of Prof. T. F. Young, the author visited his laboratory to participate with him and his student, B. M. McCarroll, in these preliminary measurements.

[21] R. H. Stokes, THIS JOURNAL, **70**, 874 (1948).

[22] The integral $\int_{m=0.1}^{m}(1-\phi)d\log m$ was evaluated from Stokes' results. Since it is equal to log $(\gamma\pm)$ at $m = 0.1$ less log $(\gamma\pm)$ at m (*cf.* R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, **45**, 612 (1949)), it is only necessary to choose one $(\gamma\pm)$ value in order to calculate the activity coefficient at any other value of m. The value chosen at $m = 0.1$ in Table III minimizes the deviation between the two sets of activity coefficients.

as does $(\gamma\pm)_{\mathrm{Na_2SO_4}}$[3] for pure sodium sulfate solutions (Fig. 2). The assumption the $(g_{\mathrm{H}^+}{}^2 g_{\mathrm{SO_4^-}})$ is similarly dependent on I in sulfuric acid–sodium sulfate solutions leads to calculated dissociation behavior which is in reasonable agreement with available experimental information. Finally, $(\gamma\pm)_{\mathrm{NaHSO_4}}$ values calculated with the additional assumption that $(g_{\mathrm{Na}^+}{}^2 g_{\mathrm{SO_4^-}}) = (g_{\mathrm{H}^+}{}^2 g_{\mathrm{SO_4^-}})$ are found to be consistent with published isopiestic results. This additional assumption is a reasonable extension of the first and, in view of the consistent $(\gamma\pm)_{\mathrm{NaHSO_4}}$ values which result, is probably justified.

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[CONTRIBUTION FROM THE MINERALS THERMODYNAMICS EXPERIMENT STATION, REGION II, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

High Temperature Heat Contents of Cryolite, Anhydrous Aluminum Fluoride and Sodium Fluoride

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High temperature heat content measurements of cryolite, anhydrous aluminum fluoride and sodium fluoride were conducted from 298.15°K. to 1370, 1401 and 1746°K., respectively. Cryolite has a crystalline transformation at 845°K. and melts at 1300°K. Aluminum fluoride has a minor crystalline transformation at 727°K. Sodium fluoride melts at 1285°K. Heat absorptions for these phase changes were extracted from the measurements. A table of heat content and entropy increments above 298.15°K., for use in thermodynamic calculations, is included.

Introduction

Despite the importance of cryolite and its constituent fluorides in aluminum metallurgy, thermodynamic data for these substances have been either lacking or inadequate. A recent paper from this Laboratory by King[1] reported the results of low temperature heat capacity measurements and entropy evaluations at 298.15°K. for cryolite, anhydrous aluminum fluoride and sodium fluoride. The present paper gives the results of high temperature heat content measurements of the same substances. The heats of formation will be the subject of a subsequent paper.

Materials.—The present work was conducted with the same samples as King[1] used in low temperature heat-capacity measurements. His paper gives the results of chemical and spectrographic analyses. It will suffice to say here that the sodium fluoride was reagent-grade material, the anhydrous aluminum fluoride was especially prepared for thermodynamic measurements, and the cryolite was hand-picked natural mineral from Greenland. The cryolite was deficient in sodium fluoride and was considered by King to be $\mathrm{Na_{2.959}AlF_{5.959}}$, for the purpose of correcting his results to stoichiometric composition. The same consideration is applied in the present work, and the reported results for cryolite have been corrected for the sodium fluoride deficiency. This correction is small in net amount, altering the results for the crystalline range by only 0.01 to 0.06% and those for the liquid range by 0.1%.

Measurements and Results.—The measurements were conducted with previously described apparatus.[2] The samples were enclosed in platinum-rhodium capsules, the heat contents of which were determined by separate experiments. After being filled with sample, each capsule was evacuated, filled with helium and sealed by platinum welding. During the course of the measurements the furnace thermocouple was calibrated frequently against the melting point of gold. Electrical calibrations of the calorimeter were in precise agreement with earlier calibrations.

The experimental heat content values are listed in Table I and plotted in Fig. 1. They are expressed in defined calories (1 cal. = 4.1840 abs. joules) per mole. Corrections to vacuum weighing were made and the employed molecular weights accord with the 1953 International Atomic Weights.[3] The definition, 0°C. = 273.15°K., was employed. The heat content values are considered accurate to within ±0.2%.

TABLE I

EXPERIMENTAL HEAT CONTENTS ABOVE 298.15°K. (CAL./MOLE)

T, °K.	$H_T - H_{298.15}$	T, °K.	$H_T - H_{298.15}$	T, °K.	$H_T - H_{298.15}$
$\mathrm{Na_3AlF_6}$ (mol. wt. 209.95)					
401.3	5,570	839.9	33,970[a]	1263.5	67,550[b]
507.8	11,740	846.7	36,000	1285.5	74,470[b]
600.2	17,410	901.4	39,600	1289.4	79,290[b]
704.1	24,090	1008.8	46,830	1296.6	85,830[b]
753.3	27,330	1052.8	49,860	1301.1	95,100
790.7	29,950	1099.8	53,070	1322.4	97,040
809.7	31,360	1152.6	57,140	1340.7	98,850
835.5	33,340[a]	1200.5	60,730	1370.5	101,650
$\mathrm{AlF_3}$ (mol. wt. 83.98)					
401.3	1,970	728.1	9,550	1045.7	17,000
500.4	4,090	736.3	9,730	1104.6	18,480
603.0	6,370	749.4	10,030	1200.4	20,810
648.4	7,440	801.6	11,240	1301.5	23,270
704.0	8,780	904.5	13,660	1379.9	25,210
714.2	9,030	1007.0	16,100	1401.2	25,800
724.9	9,320				
NaF (mol. wt. 41.99)					
406.1	1,240	1105.1	10,480	1298.0	21,460
498.1	2,360	1200.5	11,910	1313.9	21,710
602.8	3,660	1252.6	12,740	1366.3	22,580
705.2	4,970	1264.4	12,930	1428.9	23,610
800.7	6,230	1272.9	13,300	1541.9	25,490
903.6	7,610	1282.2	19,510[b]	1651.3	27,220
1003.2	9,020	1287.6	21,270	1746.5	28,780

[a] Shows pretransition effect. [b] Shows premelting effect.

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(1) E. G. King, THIS JOURNAL, **79**, 2056 (1957).

(2) K. K. Kelley, B. F. Naylor and C. H. Shomate, U. S. Bur. Mines Tech. Paper 686 (1946).

(3) E. Wichers, THIS JOURNAL, **76**, 2033 (1954).