the added salt contains common or non-common ions, providing these have the same characteristics. According to our rule this would not be true. There are no measurements for such a case.

Summary

1. New measurements of the electromotive force of the hydrogen-calomel cell with hydrochloric acid at 0.05 to 1 *M* are presented.

2. A new plot for the interpolation of activity coefficient values is shown.

3. Measurements of the electromotive force of the hydrogen-calomel cell with mixtures of hydrogen chloride with barium and lanthanum chlorides are presented.

4. The logarithm of the activity coefficient of the hydrochloric acid in mixtures of constant ionic strength is shown to be a nearly linear function of the ratio of the mean molality of the acid to the molality of pure acid at the same ionic strength.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE ACTIVITY COEFFICIENT OF SULFURIC ACID IN AQUEOUS SOLUTIONS WITH SODIUM SULFATE AT 25°

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Measurements of the electromotive force at 25° of the cell $H_2(g)$, $H_2SO_4 + Na_2SO_4(aq.)$, $Hg_2SO_4(s)$, $Hg(l)$, have been recently published by Harned and Sturgis[1] and by Åkerlöf,[2] from which the activity coefficient in solutions of low hydrogen-ion concentration were calculated. We have employed the same cell, but have used concentrations of acid and salt which enable us to calculate the activity coefficient of sulfuric acid in mixtures of all proportions up to 2 *M*.

A solution of sodium bisulfate is being used to a large extent as a substitute for sulfuric acid in many industrial processes. From these measurements, the concentration of sodium bisulfate which will give the same effective concentration as a solution of pure sulfuric acid can be calculated.

Four series of cells were measured in which the stoichiometrical molality of the sulfate ion remained constant at 0.2, 0.5, 1.0 and 2.0 *M*, respectively. In each series the molal ratio of sulfuric acid to sodium sulfate was varied.

The electrical system,[3] hydrogen electrode and mercurous sulfate electrodes were the same as those previously used in this Laboratory,

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[1] Harned and Sturgis, THIS JOURNAL, **47**, 945 (1925).

[2] (a) Åkerlöf, *ibid.*, **48**, 1160 (1926). (b) Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926).

[3] (a) Lewis, Brighton and Sebastian, THIS JOURNAL, **39**, 2245 (1917). (b) Randall and Cushman, *ibid.*, **40**, 393 (1918).

except that the platinum plates of the hydrogen electrodes were given a very light coating of platinum black.[4]

Sodium sulfate was recrystallized twice from conductivity water and kept in a desiccator. A solution of sulfuric acid was prepared by diluting a high grade, tested, pure acid to 5 *M*. This solution was analyzed both gravimetrically and volumetrically. All mixed solutions were prepared by weight from this acid and the purified sodium sulfate. Concentrations are given in moles per 1000 g. of water, all weights being corrected to vacuum.

Two cells at each concentration were made up and the difference in electromotive force of duplicate cells was always less than 0.2 mv. The electromotive force at 25° was read to 0.01 mv., and corrected to 1 atm. pressure of hydrogen. The average value of the electromotive forces for two duplicate cells is given to the nearest 0.1 mv. in Col. 4 of Table I. Col. 1 gives the total stoichiometrical molality of the sulfate ion, Col. 2 the ratio of the moles of sulfuric acid to moles of sodium sulfate, Col. 3 the square root of the ionic strength, $\mu^{1/2}$.

The activity coefficient is calculated from the relation[5]

$$\log \gamma = (\mathrm{E}^\circ - \mathrm{E})/0.088725 - \log m_\pm \qquad (1)$$

where $m_\pm$ is the mean molality of the sulfuric acid, γ is the activity coefficient of the sulfuric acid, **E** is the observed electromotive force, and **E**° is the value of the electromotive force when the activity of the sulfuric acid is unity.

From new measurements of Randall and Scott,[6] the activity coefficient of sulfuric acid at 0.0506 *M* was found to be 0.423 at 0°.

From the measurements of Brönsted[7] we may calculate values for the partial molal heat content, from which, in the dilute solutions, we obtain values of the temperature coefficient of the activity which appear unreasonably large, and which would further lower this value. This matter will receive further study, but for the present we will accept the calculations of Lewis and Randall,[8] and assume that the temperature coefficient of the activity in this dilute solution is negligible.

Åkerlöf[2] calculated the constants of the Debye-Hückel theory, employing the electromotive-force measurements of Randall and Cushman[3b] and found 0.488 for the activity coefficient at 0.05 *M*, while our value is 0.425. Åkerlöf in his calculation assumed the ordinary theory for strong electrolytes. Randall and Scott,[6] however, found sulfuric acid to be partially associated; hence, a lower value is to be expected.

[4] Harned, This Journal, **48**, 326 (1926).

[5] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Company, New York, **1923**, p. 393.

$$m_\pm = \sqrt[3]{m^2(\mathrm{H}^+)\, m(\mathrm{SO}_4^{--})}.$$

[6] Randall and Scott, This Journal, **49**, 647 (1927).

[7] Brönsted, *Z. physik. Chem.*, **68**, 693 (1910).

[8] Ref. 5, p. 354.

Randall and Cushman found $\mathbf{E}_{298} = 0.7544$ v. with pure sulfuric acid at 0.0506 *M*, whence provisionally we will take the value $\mathbf{E}^{\circ}_{298} = 0.6241$ v. Interpolating from their values, we find $\gamma = 0.262$ at 0.2 *M*, $\gamma = 0.191$ at 0.5 *M*, and 0.161 at 1.0 *M*. The values of log γ and γ, calculated by Equation 1, are given in Cols. 5 and 6 of Table I. The last column gives the value of log γ divided by the square root of the ionic strength.

Table I also contains a new value for pure sulfuric acid at 2 *M* which agrees with the interpolated value from Randall and Cushman. It also contains a single determination for a cell with equal molal mixture of zinc sulfate and sulfuric acid.[9]

TABLE I

ACTIVITY COEFFICIENTS OF SULFURIC ACID IN SODIUM SULFATE SOLUTIONS AT 25°

Total *m* of SO_4^{--}	Ratio H_2SO_4: Na_2SO_4	$\mu^{1/2}$	E.m.f., v.	Log γ	γ	$\frac{\log \gamma}{\mu^{1/2}}$
0.2	2:1	0.775	0.7313	−0.5926	0.256	−0.765
.2	1:1	.775	.7398	− .6050	.248	− .781
.2	1:3	.775	.7599	− .6309	.234	− .814
.2	1:9	.775	.7854	− .6530	.222	− .843
.5	2:1	1.225	.7087	− .7358	.184	− .601
.5	1:1	1.225	.7184	− .7619	.173	− .622
.5	1:3	1.225	.7406	− .7997	.159	− .653
.5	1:9	1.225	.7673	− .8469	.142	− .691
1.0	2:1	1.732	.6900	− .8260	.149	− .477
1.0	1:1	1.732	.7006	− .8622	.137	− .498
1.0	1:3	1.732	.7250	− .9364	.116	− .541
1.0	1:9	1.732	.7532	− .9888	.103	− .571
2.0	2:1	2.449	.6670	− .8678	.136	− .354
2.0	1:1	2.449	.6797	− .9277	.118	− .379
2.0	1:3	2.449	.7078	−1.0435	.090	− .426
1.5	1:9	2.121	.7439	−1.0599	.087	− .500
2.0	2:0	2.449	.6504	−0.7981	.159	− .326
2.0	1:1[a]	2.646	.6709	− .8285	.148	− .313

[a] Zinc sulfate instead of sodium sulfate.

The values of the activity coefficient are plotted against the square root of the ionic strength in Fig. 1. The broken curve F represents the activity coefficient of sulfuric acid in a sodium sulfate solution in which the concentration of the hydrogen ion is very small. The points through which it is drawn are taken from Fig. 3.

The dotted curve G, where the molality of the sulfuric acid is 0.1, was constructed by drawing through Curve C at $\mu = 0.6$, through Curve E at $\mu = 3.0$, and through the dotted points at $\mu = 1.5$ and 6.0. The dotted points were calculated by means of the curves of Fig. 3. In a similar manner we have drawn Curve H, where $H_2SO_4 = 0.05$ *M*, through Curve D at $\mu = 0.6$, and through Curve E at $\mu = 0.3$.

The points of Harned and Sturgis[1] at $H_2SO_4 = 0.1$ *M*, recalculated

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[9] For this measurement we are indebted to Miss Mary G. Atkinson.

to E°_{298} = 0.6241 v., are shown by shaded circles and at 0.01 *M* by half-shaded circles. It is seen that the 0.1 *M* points are in fair agreement with our measurements. The agreement of the 0.01 *M* points is not so good. They appear to be uniformly high.

Åkerlöf[2] used concentrations rather than molalities; hence, it is impossible to make a complete comparison with his results. He was probably influenced in his use of concentration by the fact that the development of the Debye-Hückel theory is in concentrations rather than in molalities. The practical reason for adopting molality rather than concentration still exists, namely, the concentration of a solution changes with temperature owing to the expansion of the solution. It is hoped, therefore, that investigators will continue to use molalities in thermodynamic work, or determine the density of the solutions used.

We have recalculated Åkerlöf's values for the activity coefficient for concentrations, γ_c, ($\gamma_c = a_{\pm}/c_{\pm}$) to E° = 0.6241 v. The shaded squares in Fig. 1 represent sulfuric acid, c = 0.05, and the half-shaded squares represent c = 0.005. The deviation due to the use of concentration units is greater in the more concentrated solutions. Taking this into consideration, Åkerlöf's[2] values at 0.05 are in fair agreement with Curve H, and his values at 0.005 are in better agreement with our values than are the 0.01 *M* values of Harned and Sturgis.

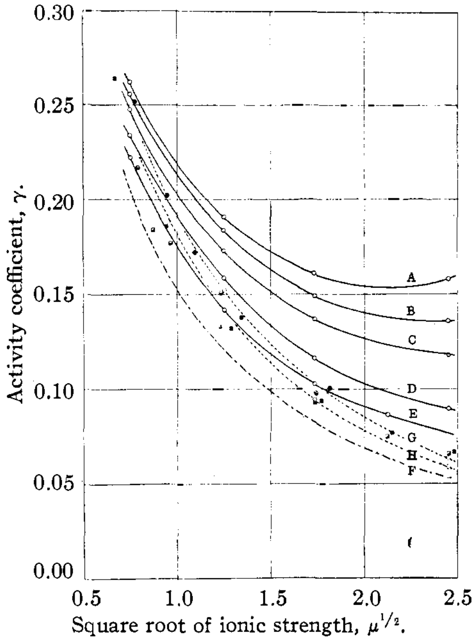

Fig. 1.—The activity coefficient of aqueous sulfuric acid in mixtures with sodium sulfate at 25°. A, pure H_2SO_4; B, 2 H_2SO_4 : 1 Na_2SO_4; C, 1 H_2SO_4 : 1 Na_2SO_4; D, 1 H_2SO_4 : 3 Na_2SO_4; E, 1 H_2SO_4 : 9 Na_2SO_4; F, 1 H_2SO_4 : ∞ Na_2SO_4; G, H_2SO_4, *m*, 0.1; H, H_2SO_4, *m*, 0.05. ●, H and S, H_2SO_4, *m*, 0.1; ◒, H and S, H_2SO_4, *m*, 0.01; ■ A, H_2SO_4, *c*, 0.05; ◪, A, H_2SO_4, *c*, 0.005.

Our data are also shown in Fig. 2, in which the values of $(\log \gamma)/\mu^{1/2}$ are plotted against the square root of the ionic strength.

Randall and Breckenridge[10] found that with similar plots for mixtures of hydrochloric acid and barium chloride, and hydrochloric acid and lanthanum chloride, the curves pointed very closely to the Debye-Hückel limit, which is approximately —0.513 for uni-univalent electrolytes. Our

[10] Randall and Breckenridge, THIS JOURNAL, **49**, 1435 (1927).

curves are more nearly parallel than those of Randall and Breckenridge. Sulfuric acid, however, is not fully dissociated. The addition of sulfate ions tends to depress this dissociation in accordance with the mass law. Since the effect of a lower dissociation is to decrease the activity coefficient, the trend of our curves is in the expected direction.

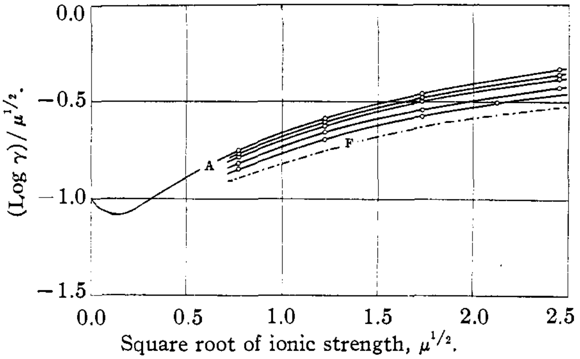

Fig. 2.—The activity coefficient of aqueous sulfuric acid in mixtures with sodium sulfate at 25°. A, pure H_2SO_4; B, 2 H_2SO_4 : 1 Na_2SO_4; C, 1 H_2SO_4 : 1 Na_2SO_4; D, 1 H_2SO_4 : 3 Na_2SO_4; E, 1 H_2SO_4 : 9 Na_2SO_4; F, 1 H_2SO_4: ∞ Na_2SO_4.

Up to this point when we have spoken of the molality of sulfuric acid we have followed the usual custom of referring to one-half the stoichiometrical molality of the hydrogen ion. However, the effective molality of sulfuric acid is the geometrical average of the molality of the hydrogen and sulfate ions. The extent to which the ionic-strength principle is obeyed is shown effectively in Fig. 3, in which the logarithms of the activity coefficients are plotted against the ratios of the average molality of the sulfuric acid to the average molality of sulfuric acid in a solution of pure sulfuric acid of the same ionic strength as that of the mixture. If the principle of the ionic strength were true, the curves of Fig. 3 would be horizontal straight lines. The principle is best obeyed in the more dilute solutions, and when the fraction of the average molality of sulfuric acid is large. This is in accord with the limitations of the principle as first stated by Lewis and Randall.

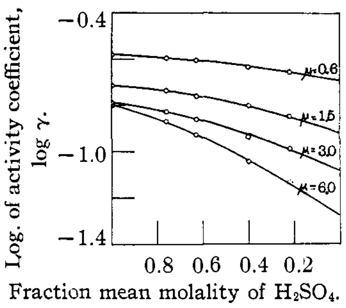

Fig. 3.—Change of the activity coefficient of sulfuric acid with the fraction of average molality.

Åkerlöf calculated the constants of the Debye-Hückel equation, assuming sulfuric acid to be a strong electrolyte, and with similar constants for sodium sulfate showed that his results were in agreement with Hückel's treatment of mixtures. In effect, he assumed that the limit of $(\log \gamma)/\mu^{1/2}$ was —1.0, and that the approach to this limit was without the minimum shown in Fig. 2. His other constants are empirical, but the new form of the curve at the dilute end would require some revision of these constants which, so long as they fitted the results for pure acid, would probably fit the mixtures just as well. We have not attempted to calculate such constants.

We have also plotted the logarithm of the activity coefficient against the ratio of the ionic strength of the sulfuric acid by the total ionic strength, as indicated by the rule of Åkerlöf[2a] and of Harned and Åkerlöf.[2b] We find that the curvature is greater than that of the curves shown in Fig. 3.

The activity coefficient in the presence of magnesium sulfate as measured by Harned and Sturgis[1] is in much better agreement with the principle of the ionic strength. In the mixture with zinc sulfate the rule is also closely obeyed. The freezing point function, $j/m^{1/2}$, of magnesium and zinc sulfates shows the same sort of a divergence in dilute solution as that found by Randall and Scott[6] for barium nitrate. They are, therefore, in this sense to be regarded as slightly weak salts. We may expect the ionic-strength rule to apply better in the case of mixtures of the slightly weak sulfuric acid with these substances than with the typically strong sodium sulfate.

Summary

Measurements of the hydrogen-mercurous sulfate cell have been made, in which the electrolyte consisted of sulfuric acid and sodium sulfate in varying proportions.

Assuming a provisional value $\mathbf{E}^{\circ}_{298} = 0.6241$ v. for the mercurous sulfate electrode, the activity coefficients of sulfuric acid have been calculated.

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