which large positive and negative currents were in the circuit, and during which time the sign and magnitude of the electrode potential probably changed. It therefore appears impossible to say at which potential the oxygen was liberated, and in the absence of evidence to the contrary it is simpler to assume that this gas was liberated when the potential of the electrode was equal to or greater than the reversible value. The same argument applies to the results of Goodwin and Knobel[2f] in connection with the liberation of hydrogen at a lead cathode in sulfuric acid.

Summary

The reasons are outlined for believing that many of the potentials given in the literature, which purport to indicate the influence of alternating current on overvoltage, are of doubtful value. The effect of small alternating currents on cathodic and anodic overvoltage has been measured approximately for a number of different metals in *N* sulfuric acid and *N* sodium hydroxide solutions. The results indicate that only in a limited number of cases does alternating current of small amplitude reduce the polarization at such electrodes. A possible explanation for the effect of alternating current in lowering overvoltage in some cases is discussed briefly.

EXETER, ENGLAND

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF THE UNIVERSITY OF PENNSYLVANIA]

THE FREE ENERGY OF SULFURIC ACID IN AQUEOUS SULFATE SOLUTIONS

BY HERBERT S. HARNED AND RUSSELL D. STURGIS

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The free energy of dilution of sulfuric acid in aqueous solutions may be computed accurately at concentrations above 0.01 *M* concentration from measurements of the electromotive forces of cells of the type,

$$H_2 \mid H_2SO_4(m) \mid Hg_2SO_4 \mid Hg$$

where m is the molal concentration. These cells have been studied by Brönsted[1] who extended his measurements over a considerable concentration range and at different temperatures, Lewis and Lacy,[2] and more recently by Randall and Cushman.[3] The results of these studies along with freezing-point measurements and the vapor-pressure measurements of Brönsted[1] have been employed by Lewis and Randall[4] for their computation of the activity coefficients of this acid.

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

[2] Lewis and Lacy, THIS JOURNAL, **36**, 804 (1914).

[3] Randall and Cushman, *ibid.*, **40**, 393 (1918).

[4] Lewis and Randall, (a) *ibid.*, **43**, 1112 (1921). (b) "Thermodynamics," McGraw-Hill Book Co., **1923**, p. 355.

Measurements of the electromotive forces of cells of the type,

$$H_2 \mid HCl(m_1), MeCl_x(m) \mid HgCl \mid Hg$$

where $MeCl_x$ represents either an alkali or an alkaline-earth metal chloride have been carried out by Loomis, Essex and Meacham,[5] Chow,[6] Harned,[7] and Harned and Brumbaugh,[8] from which it is possible to compute the activity coefficients of hydrochloric acid in the salt solutions. Since no similar data were available on cells containing an electrolyte of a higher valence type, measurements of the electromotive forces of cells of the types,

$$H_2 \mid H_2SO_4(m_1), Me_2^ISO_4 \mid Hg_2SO_4 \mid Hg \text{ and } H_2 \mid H_2SO_4(m_1), Me^{II}SO_4 \mid Hg_2SO_4 \mid Hg$$

where Me^I represents sodium or potassium, and Me^{II} represents magnesium, have been made, and from these the activity coefficients of the sulfuric acid in the sulfate solutions computed.

Materials and Procedure

Since careful descriptions of these types of cells and their measurement have been given many times in the investigations to which reference has been made, only the methods of preparation of the materials employed and some essential precautions will be described here.

Four times distilled mercury was employed. The mercurous sulfate was prepared electrolytically from a portion of this mercury by the method of Hulett.[9] It was not pure white, but very slightly grayish owing to the presence of very finely divided mercury. The electromotive forces of electrodes prepared from samples of this material which were made at different times differed from one another by less than 0.05 mv.

The sodium and potassium sulfates were crystallized and centrifuged from ordinary distilled water until their solutions gave no test for the chloride ion. They were then recrystallized twice from redistilled water. Approximately 100g. portions were ignited to dull redness in platinum, kept at that temperature for ten minutes, and then transferred to a vacuum desiccator. The solutions were made by weighing suitable portions.

The magnesium sulfate was recrystallized twice from redistilled water. A nearly saturated solution was then made and carefully analyzed gravimetrically. All other solutions of this salt were prepared by weighing portions of this solution.

A solution of sulfuric acid was prepared by diluting the pure acid to a concentration of approximately 4 *M*. This was carefully analyzed gravimetrically so that the acid content was known to less than 0.05% of the total acid. All solutions were made from this acid by the weight method. Molal concentrations (formula weights per 1000 g. of water) were employed throughout.

Some precautions regarding the mercurous sulfate electrode should be mentioned. In these measurements, great care was exercised in preventing the platinum lead-in wire from becoming wetted by the solution. The electrode vessel was carefully dried and the platinum lead was covered with mercury. The mercurous sulfate was then introduced after it had been

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[5] Loomis, Essex and Meacham, THIS JOURNAL, **39,** 1133 (1917).

[6] Chow, *ibid.*, **42,** 497 (1920).

[7] Harned, *ibid.*, **38,** 1986 (1916); **42,** 1808 (1920).

[8] Harned and Brumbaugh, *ibid.*, **44,** 2729 (1922).

[9] Hulett, *Phys. Rev.*, **32,** 257 (1911).

washed by decantation six times with the solution to be employed in the cell. Our experience in this respect was fully in accord with that of Randall and Cushman[3] who observed that highly reproducible results could not be obtained if the above precaution was not observed.

It is known that the mercurous sulfate electrode is not reliable in the very dilute solutions (below 0.005 *M*). Lewis and Randall[10] attribute this behavior to the solubility of mercurous sulfate. Beside this, in the acid solutions of concentrations somewhat below 0.01 *M*, indications of the formation of the yellow basic sulfate are observable. Either one or both of these factors may be responsible for this lack of reliability.

Experimental Results

In Table I are given the electromotive forces of the cells,

$$H_2 \mid H_2SO_4(0.1), Me_xSO_4\ (m) \mid Hg_2SO_4 \mid Hg$$

TABLE I

ELECTROMOTIVE FORCES OF THE CELLS

$H_2 \mid H_2SO_4(0.1), Me_xSO_4(m) \mid Hg_2SO_4 \mid Hg$

	$Me_x = K_2$	$Me_x = Na_2$	$Me_x = Mg$
m	E_{25}	E_{25}	E_{25}
0.00	0.73724	0.73724	0.73724
.00	.73720	.73720	.73720
.10	.74021	.73933	.73849
.10	....	....	.73837
.20	.74439	.74251	.73991
.30	.74768	.74505	.74090
.50	.75341	.74840	.74205
1.00	....	.75237	.74193
1.00	....	....	.74199

TABLE II

ELECTROMOTIVE FORCES OF THE CELLS

$H_2 \mid H_2SO_4(0.01), Me_xSO_4(m) \mid Hg_2SO_4 \mid Hg$

	$Me_x = K_2$	$Me_x = Na_2$	$Me_x = Mg$
m	E_{25}	E_{25}	E_{25}
0.0	0.79694	0.79694	0.79694
.0	.79711	.79711	.79711
.0	.79713	.79713	.79713
.02	.79529	.79501	.79526
.03	.79578	....	....
.05	.79704	.79628	.79610
.09	.80001	.79899	....
.1	.80050	.79947	.79755
.2	.80551	.80353	.79979
.3	.80874	.80619	.80125
.5	.81431	.80897	.80246
.5	.81454	....	....
1.0	....	.81404	.80183

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[10] Ref. 4 b, p. 356.

at 25°. All concentrations are expressed in moles per 1000 g. of water; E, the electromotive force, is corrected to 1 atm. hydrogen pressure.

In Table II are given the similar series of results of the electromotive forces of the cells, $H_2 \mid H_2SO_4$ (0.01), $Me_xSO_4(m) \mid Hg_2SO_4 \mid Hg$, at 25°.

In these Tables the results that are in duplicate or triplicate were made at different times and with different materials.

Table III contains the results with the cells,

$$H_2 \mid H_2SO_4(m_1),\ Me_xSO_4(m) \mid Hg_2SO_4 \mid Hg$$

at constant total molality where $(m + m_1)$ equals 0.1.

Table III

Electromotive Forces of the Cells

$H_2 \mid H_2SO_4(m_1),\ Me_xSO_4(m) \mid Hg_2SO_4 \mid Hg$

$(m + m_1) = 0.1$

m_1	0.100	0.07	0.05	0.03	0.02	0.01	0.003
$Me_x = K_2$	.73722	.74662	.75600	.77031	.78134	.80001	.83114
$Me_x = Na_2$	.73722	.74617	.75550	.76960	.78029	.79899	.83003

Calculation of the Activity Coefficients

If the value of the electromotive force of the cell containing both salt and acid be subtracted from that of the cell containing acid at a given acid concentration, the electromotive force, ΔE, corresponding to the process of transfer of the acid from the salt solution to the solution of the pure acid, is obtained. This electromotive force is related to the activities of the ions of the acid by the well-known thermodynamic equation

$$\Delta E = \frac{RT}{2\,F} ln \frac{a^2{}_{H(s)}\ a_{SO_4(s)}}{a^2{}_H\ a_{SO_4}} = \frac{3}{2}\frac{RT}{F} ln \frac{\sqrt[3]{a^2{}_{H(s)}\ a_{SO_4(s)}}}{\sqrt[3]{a^2{}_H\ a_{SO_4}}}$$

$$= \frac{3}{2}\frac{RT}{F} ln \frac{a_{\pm(s)}}{a_{\pm}} = 0.08872 \log \frac{a_{\pm(s)}}{a_{\pm}} \qquad (1)$$

where (s) refers to the solution, $a_{\pm(s)}$ is the cube root of the activity product of the acid in the solution which contains the salt and $a_{\pm}$ is the cube root of the activity product of the acid in the solution which does not contain the salt. Thus, if $a_{\pm}$ is known, $a_{\pm(s)}$ may be calculated. The activity coefficient of the acid, γ, in the salt solutions may then be computed by the equation

$$\gamma = \frac{a_{\pm(s)}}{(m^2{}_H\ m_{SO_4})^{\frac{1}{3}}} \qquad (2)$$

Therefore, to calculate γ from these results, it is necessary to know its value in a solution of the acid at either 0.1 or 0.01 M concentration.

Both the values of the electromotive forces of the cells containing 0.1 and 0.01 M acid and without salt fall on the curve of the results of Randall and Cushman.[3] The result at 0.01 M acid concentration is somewhat lower than that obtained by Brönsted.[1] For the calculation of the activity coefficients, the value of 0.313 at 0.1 M acid, taken from the calculation of Lewis and Randall[10] has been employed. From this value and the electromotive forces given above, it is found that the activity coefficient of the acid at 0.01 *M* is 0.662, a value in disagreement with that obtained by Lewis and Randall from freezing-point data. As mentioned by these investigators, this lack of agreement may be caused by the unreliability of the mercurous sulfate electrode in the 0.01 *M* acid solution, even though it was found that these cells were reproducible to within 0.1 mv., and this series of measurements show a high order of consistency. On the other hand, it is possible that the freezing-point measurements employed by Lewis and Randall in their calculation are inaccurate in the region between 0.01 and 0.1 *M* concentrations. For the sake of consistency, we have employed the value 0.662 for γ at 0.01 *M* acid concentration. In Table IV are given the results of this calculation. The salt concentration, *m*, the activity coefficient, γ, and the ionic strength, μ, as defined by Lewis and Randall, have been included.

Table IV

The Activity Coefficients of Sulfuric Acid in Sulfate Solutions

0.1 *M* Acid

		K_2SO_4	Na_2SO_4	$MgSO_4$	
m	μ	γ	γ	μ	γ
0.0	0.30	0.313	0.313	0.30	0.313
.1	.60	.230	.235	.70	.241
.2	.90	.180	.190	1.1	.202
.3	1.20	.150	.161	1.5	.179
.5	1.80	.113	.129	2.3	.152
1.0	3.30	..	.095	4.3	.124
0.01 *M* Acid					
0.0	0.03	0.662	0.662	0.03	0.662
.02	.09	.481	.484	.11	.481
.03	.12	.431	..	..	..
.05	.18	.365	.372	.23	.374
.09	.30	.285	.292	..	..
.10	.33	.272	.280	.43	.294
.20	.63	.193	.203	.83	.224
.30	.93	.156	.166	1.23	.189
.50	1.53	.114	.131	2.03	.155
1.00	3.03	..	.092	4.03	.126

In Fig. 1, the values of the activity coefficients of the acid in the sulfate solutions are plotted against the ionic strength as well as the activity coefficients of the acid in aqueous solution taken from the table of Lewis and Randall.[11] The ordinates of γ of the 0.01 *M* and 0.1 *M* series are on the left and right, respectively. The activity coefficient of the acid in the potassium sulfate solutions is less than in the sodium sulfate solutions. Further, the activity coefficient in these solutions is considerably less than in solutions of the pure acid. The behavior of sulfuric acid is thus similar to

[11] Ref. 4b, p. 362.

that of hydrochloric acid in solutions of potassium and sodium chlorides.[12] This is further evidence for the fact that in a salt solution containing an acid or an hydroxide the hydrogen-ion activity is always greater in a solution containing the sodium ion than in one containing the potassium ion. Evidence that this is true in sulfate solutions of 0.05 *N* sulfuric acid has been obtained by Åkerlöf.[13] The values for the activity coefficients of the acid in the magnesium sulfate solutions are near those of the acid in pure aqueous solution. In the less concentrated solutions, they are somewhat higher, in the more concentrated solutions lower. They are higher than the values in the sodium and potassium sulfate solutions, a fact also in agreement with the results of Åkerlöf. There is another question of interest which should be mentioned. A uni-bivalent acid (sulfuric) will have a much lower activity coefficient than a uni-univalent acid (hydrochloric) at a given concentration or ionic strength, whether in an aqueous solution or in a salt solution. This follows from a consideration of valence types of the electrolytes involved. Thus, starting with a given concentration of the electrolyte, the addition of a salt would decrease the ion activities in the uni-bivalent solutions much more than in the uni-univalent solutions. Indeed, the activity coefficient of a uni-univalent electrolyte such as hydrochloric acid begins to increase above a certain concentration. From these considerations, it is clear that the addition

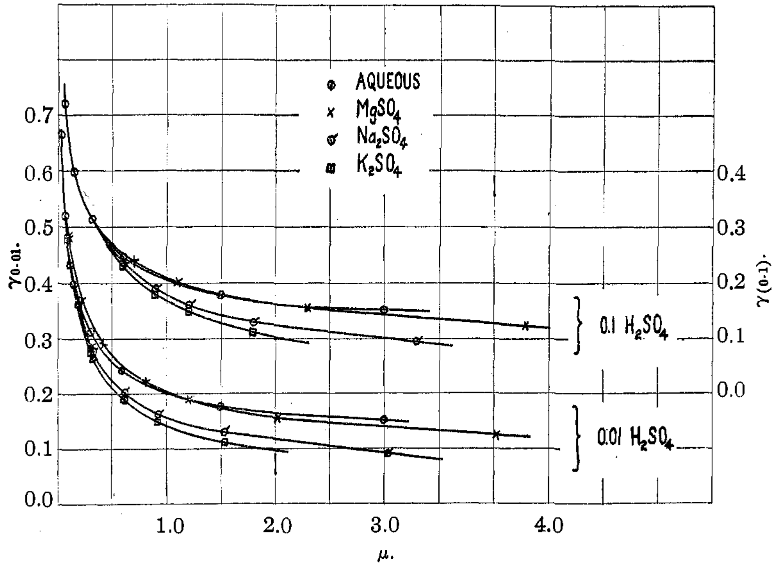

Fig. 1.—Activity coefficient of 0.01 and 0.1 *M* sulfuric acid in sulfate solutions.

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[12] Harned, This Journal, **42**, 1808 (1920). Ref. 8.

[13] Åkerlöf, *Z. physik. Chem.*, **98**, 260 (1921).

of a uni-univalent salt to hydrochloric acid at a concentration not too dilute may increase its hydrogen-ion activity, while the addition of a uni-bivalent salt to sulfuric acid at the same concentration may decrease the hydrogen-ion activity. This is in agreement with the results of Harned[14] who found that the addition of chlorides to 0.1 *M* hydrochloric acid increased the activity of the hydrogen ion, and by Åkerlöf who found that the same was true with 0.05 *M* hydrochloric and nitric acids but that the addition of potassium, sodium and magnesium sulfates decreased, at first very rapidly, the hydrogen-ion activity of sulfuric acid.

The Activity Coefficients at Constant Total Molality

From the electromotive-force data in Table III, and by means of Equations 1 and 2, it is possible to compute the activity coefficient of the acid in potassium and sodium sulfate solutions at 0.1 total molal concentration. The results of such a calculation are given in Table V. The rows contain the molal acid concentration, the activity coefficient of the acid and its logarithm, respectively.

TABLE V

ACTIVITY COEFFICIENTS OF SULFURIC ACID IN SULFATE SOLUTIONS AT 0.1 *M* TOTAL CONCENTRATION

m_1	0.003	0.010	0.020	0.030	0.050	0.070	0.100
POTASSIUM SULFATE							
γ	.2832	.2847	.2911	.2958	.3051	.3111	.313
Log γ	−1.4521	.4544	.4641	.4710	.4844	.4927	.4955
SODIUM SULFATE							
γ	0.2915	0.2923	0.2992	0.3013	0.3090	0.3146	
Log γ	−1.4646	.4659	.4760	.4791	.4901	.4978	

Electromotive-force measurements of a similar nature have been made. Loomis, Essex and Meacham[5] found a slight decrease in the activity coefficient of hydrochloric acid in potassium chloride solutions in going from 0.1 to 0.01 *M* acid. Chow,[6] who extended the series from 0.01 to 0.0001 *M*, concluded from his results that the activity coefficient remained constant throughout that range. However, his results fell off slightly between 0.1 and 0.01 *M* acid concentration. This was also observed by Harned and Brumbaugh.[8] It is a point of considerable interest to find out whether the logarithm of the activity coefficient varies linearly with the concentration of the acid at total molal concentration. That this is approximately true for hydrochloric acid in potassium chloride mixtures in the region of 0.01 to 0.1 *M* was shown by Harned and Brumbaugh. Brönsted[15] has also obtained much evidence for such a linear variation for other electrolytes in other solvents from solubility data in solutions under 0.1 *M* total con-

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[14] Harned, THIS JOURNAL, **37**, 2460 (1915). Ref. 7.

[15] Brönsted, *ibid.*, **44**, 877 (1922); **45**, 2898 (1923).

centration. In Fig. 2, are plotted the values of the logarithm of the activity coefficients for sulfuric acid in the presence of potassium sulfate and sodium sulfate against the concentration of sulfuric acid at a constant total molality of 0.1. From the present careful measurements the linear relation does not hold in the region between 0.07 and 0.1 *M* acid concentrations but appears to hold with considerable exactness in the region of 0.003 to 0.06 *M* sulfuric acid concentration. Although this does not prove that an exact linear relationship exists, it is evidence that the activity coefficient of the acid does not remain constant in a solution of this total ionic strength.

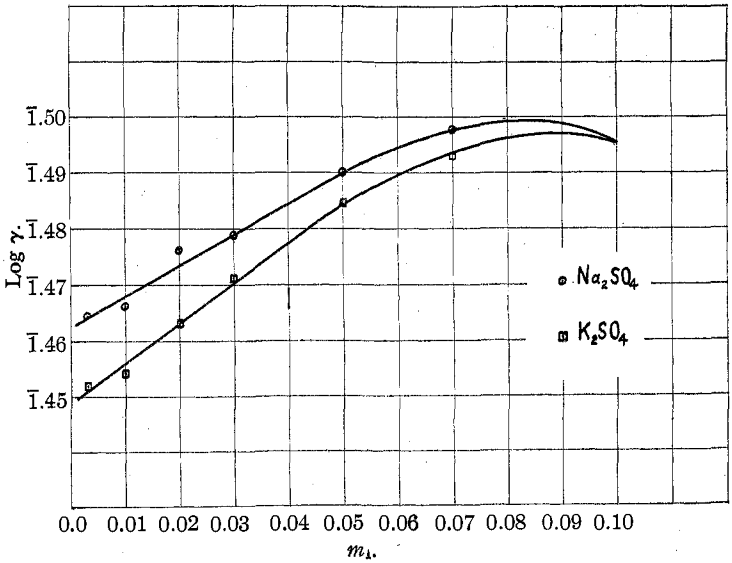

Fig. 2.—Activity coefficient of sulfuric acid at constant total molality.

Summary

1. Measurements were made of the electromotive forces of the cells

$$H_2 \mid Me^{I}SO_4(m) \text{ in } H_2SO_4(0.01) \mid Hg_2SO_4 \mid Hg$$

and

$$H_2 \mid Me^{II}SO_4(m) \text{ in } H_2SO_4\ (0.01) \mid Hg_2SO_4 \mid Hg$$

at 25°, where Me^{I} was Na or K and Me^{II} was Mg.

2. Measurements were made of the cells

$$H_2 \mid Me^{I}SO_4(m) \text{ in } H_2SO_4\ (0.1) \mid Hg_2SO_4 \mid Hg$$

and

$$H_2 \mid Me^{II}SO_4(m) \text{ in } H_2SO_4\ (0.1) \mid Hg_2SO_4 \mid Hg$$

at 25°.

3. Measurements were made of the cells

$$H_2 \mid H_2SO_4(m),\ Me_2{}^{I}SO_4(m_1) \mid Hg_2SO_4 \mid Hg$$

where $(m + m_1)$ was kept at 0.1 M concentration, and both the acid and salt concentrations were varied.

4. From these measurements, the activity coefficients of the acid in these different solutions were computed.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE LABORATORIES OF GENERAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE DECOMPOSITION OF MALIC ACID BY SULFURIC ACID[1]

BY EARL L. WHITFORD

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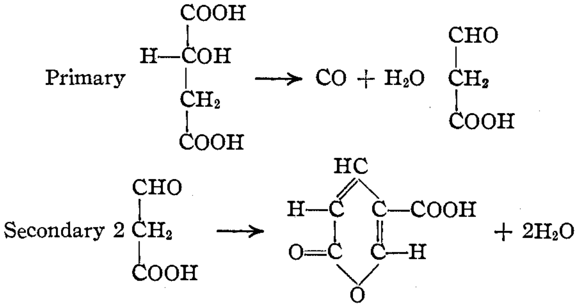
Introduction

While dehydration reactions by sulfuric acid have been studied to a considerable extent, Bredig and Lichty[2] were the first to measure the velocity of such a reaction and study systematically the effect of varying the concentrations of the acid. Later, Schierz[3] made a similar study of the decomposition of formic acid. Both of these reactions may be looked upon as straight dehydration reactions according to the following equations: $(COOH)_2 \longrightarrow CO + CO_2 + H_2O$; $HCOOH \longrightarrow CO + H_2O$. Subsequent considerations, however, point to a more complex mechanism which will be discussed later.

Dobereiner[4] observed that malic acid is decomposed by concd. sulfuric acid with the evolution of carbon monoxide. This reaction was later studied by v. Pechmann[5] who showed that the reaction is quantitative in concd. sulfuric acid solutions and takes place in two steps. The two reactions may be represented by the following reactions.



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[1] The work included in this paper is from the thesis presented by Earl L. Whitford in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin. This investigation was conducted under the supervision of Professor J. H. Walton.

[2] Bredig and Lichty, *Z. Elektrochem.* **12**, 459 (1906); *J. Phys. Chem.*, **11**, 255 (1907).

[3] Schierz, THIS JOURNAL, **45**, 447 (1923).

[4] Dobereiner, *Schweigger's J. Chem. Phys.*, **26**, 276 (1819).

[5] v. Pechmann, *Ber.*, **17**, 929, 936 (1884).