

TABLE III

THE PARTIAL MOLAL VOLUMES OF CALCIUM NITRATE AND OF WATER IN AQUEOUS SOLUTIONS AT 25°

<i>m</i>	<i>d</i>	<i>V</i> <sub>obs.</sub> , cc.	$\Delta V$ , cc.	$\bar{v}_2$ , cc.	$\bar{v}_1$ , cc.
0.0	0.997071	1002.938	-0.024	37.526	18.068
.1	1.009670	1006.664	-.072	37.959	18.066
.2	1.022093	1010.494	-.060	38.392	18.065
.4	1.046507	1018.281	-.124	39.258	18.061
.6	1.070371	1026.239	-.018	40.123	18.054
.8	1.093683	1034.373	-.005	40.989	18.043
1.0	1.116449	1042.676	.013	41.875	18.029
1.5	1.170956	1064.210	.089	44.019	17.982
2.0	1.222150	1086.766	.095	46.183	17.914
2.5	1.270014	1110.410	.106	48.347	17.826
3.0	1.314619	1135.148	.130	50.511	17.720
3.5	1.356078	1160.948	.134	52.675	17.593
4.0	1.394473	1187.820	.127	54.839	17.447
5.0	1.462485	1244.785	.089	59.167	17.095
6.0	1.519536	1306.040	.013	63.495	16.666
7.0	1.566558	1371.587	-.099	67.823	16.156
8.0	1.604500	1441.426	-.247	72.151	15.569
8.3601 <sup>a</sup>	1.616059	1467.619	-.314	73.710	15.338

<sup>a</sup> Saturated.

TABLE IV

THE PARTIAL MOLAL VOLUMES OF ALUMINUM NITRATE AND OF WATER IN AQUEOUS SOLUTIONS AT 25°

<i>m</i>	<i>d</i>	<i>V</i> <sub>obs.</sub> , cc.	$\Delta V$ , cc.	$\bar{v}_2$ , cc.	$\bar{v}_1$ , cc.
0.0	0.997071	1002.938	-0.135	52.890	18.068
.1	1.012725	1008.471	.058	53.908	18.068

0.2	1.028301	1013.904	0.049	54.926	18.067
.4	1.058649	1025.077	.034	56.961	18.056
.6	1.087913	1036.659	.020	58.997	18.037
.8	1.116096	1048.651	.009	61.033	18.012
1.0	1.143200	1061.051	-.001	63.069	17.978
1.5	1.206298	1093.842	-.017	68.158	17.864
2.0	1.262843	1129.188	-.022	73.247	17.703
2.5	1.313080	1167.092	-.014	78.337	17.497
3.0	1.357277	1207.551	.004	83.428	17.245
3.1067 <sup>a</sup>	1.370250	1221.098	.013	85.062	17.154

<sup>a</sup> Saturated.

### Summary

The vapor pressures of aqueous solutions of calcium nitrate and of aluminum nitrate at 25° have been measured for concentrations ranging from 0.1 *m* to the saturated solution in contact with the solid crystals.

From the vapor pressure data we have calculated the activity of the solvent and the activity coefficients of the ions at each concentration, and the free energy of dilution of both the solute and the solvent. The partial molal volumes of the solvent and salts have been calculated.

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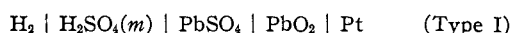
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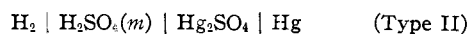
## The Thermodynamics of Aqueous Sulfuric Acid Solutions from Electromotive Force Measurements<sup>1</sup>

BY HERBERT S. HARNED AND WALTER J. HAMER

In a recent communication<sup>2</sup> a very comprehensive series of measurements of the cells



from 0 to 60° and throughout a concentration range from 0.0005 to 7 *M* was made, and from these the molal electrode potentials of the lead sulfate-lead dioxide electrodes were computed. These results have been supplemented by measurements of the cells



through the same temperature range and through a concentration range of 0.05 to 17.5 *M*. From the combination of these results, the vapor pressures of the solutions, the activity coefficient of

sulfuric acid, the relative partial molal heat content and relative partial molal specific heat of sulfuric acid in aqueous solutions, have been computed throughout the entire concentration and temperature ranges. The molal electrode potential of the mercurous sulfate-mercury electrode has also been evaluated.

### Experimental Results

Since the measurements of cells I have already been reported, it is necessary to give only the results of cell II. The apparatus was that described by Hamer.<sup>2</sup> Twice distilled mercury was employed. The mercurous sulfate was prepared by the electrolytic method of Hulett<sup>3</sup> which yields a preparation of fine grains and which shows little or no hysteresis and hydrolyses to a lesser degree than other preparations. This material was di-

(1) This contribution is part of an investigation of the thermodynamic properties of the electrodes and electrolyte of the lead accumulator. This work was made possible by a grant from the Naval Research Laboratory, Anacostia Station, Washington, D. C., and is published with permission of the Secretary of the Navy.

(2) Hamer, *This Journal*, **57**, 9 (1935).

(3) Hulett, *Phys. Rev.*, **32**, 257 (1911).

gested with 3 *M* sulfuric acid as recommended by Vosburgh and Eppley,<sup>4</sup> and the final preparation was kept under 0.02 *M* sulfuric acid in the absence of light until used. The electrodes were prepared in the usual manner. The observation of Randall and Cushman<sup>5</sup> that concentrated sulfuric acid solutions are not reduced at the hydrogen electrode was confirmed.

The electromotive forces of the cells were constant and as a rule were reproducible to  $\pm 0.05$  mv. although the maximum deviation was  $\pm 0.1$  mv. Constancy was obtained to concentrations as low as 0.002 *M*. At lower concentrations hydrolysis occurs and the basic sulfate is formed. Hysteresis was not observed but in order to be certain of its elimination measurements were made after an increase in temperature and not after a decrease. Since, due to the action of light, a yellow basic sulfate appears after two or more days, measurements were made in the course of a day. New electrodes were employed for all measurements and even though a vacuum technique is unnecessary, the cells were filled *in vacuo*.

We have not included the results at concentrations below 0.05 *M*. Although constancy was obtained, the solubility of mercurous sulfate becomes a disturbing factor. Corrections for this effect are difficult. The total sulfate ion concentration may be computed as described by Hamer but the effect of the mercurous ion which is not definitely known cannot be neglected. Further, since the hydrogen electrode must be kept in a solution which does not contain mercurous ions, an appreciable liquid junction potential may be present.

Since measurements were made at 5° intervals from 0 to 60° and at so many concentrations any completed tabulation of the results would be bulky. For the sake of brevity, the results were smoothed by the method described by Hamer and the electromotive forces at round concentrations were obtained. These may be expressed as a function of temperature within the limit of experimental accuracy by the quadratic equation

$$E' = E_{25} + a(t - 25) + b(t - 25)^2 \quad (1)$$

where  $E'$  is the electromotive force at the temperature  $t$ ,  $E_{25}$  that at 25°, and  $a$  and  $b$  are constants. The values of  $E_{25}$  corrected to one atmosphere pressure and the values of  $a$  and  $b$  are given in

(4) Vosburgh and Eppley, *THIS JOURNAL*, **46**, 104 (1924); **45**, 2268 (1923); Summers and Gardiner, *Trans. Am. Electrochem. Soc.*, **56**, 18 (1929); Gardiner and Hulett, *ibid.*, **46**, 17 (1919).

(5) Randall and Cushman, *THIS JOURNAL*, **40**, 393 (1918).

Table I. The constants of the equations were derived from the results at the thirteen temperatures from 0 to 60° by the method of least squares.

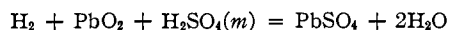
TABLE I

THE ELECTROMOTIVE FORCES OF THE CELL,  $\text{H}_2 | \text{H}_2\text{SO}_4(m) | \text{Hg}_2\text{SO}_4 | \text{Hg}$  AT 25° AND CONSTANTS OF EQUATION (1),  
 $E' = E_{25} + a(t - 25) + b(t - 25)^2$

$m(\text{H}_2\text{SO}_4)$	$E_{25}$	$-a \times 10^6$	$b \times 10^6$
0.05	0.75434	10.0	-5.83
.10	.73714	31.7	-3.47
.20	.71970	73.05	-2.72
.50	.69609	139.94	-1.33
1.00	.67600	185.77	6.22
1.50	.66213	216.35	9.47
2.00	.65088	235.0	10.31
3.00	.63041	241.8	11.74
4.00	.61201	240.6	13.01
5.00	.59498	234.3	14.27
6.00	.57952	232.3	15.83
7.00	.56550	226.8	16.89
8.00	.55289	221.7	21.16
9.00	.54153	215.4	29.44
10.00	.53149	209.8	32.73
11.00	.52189	203.3	36.57
12.00	.51304	199.1	38.59
13.00	.50475	196.0	31.98
14.00	.49688	187.0	29.09
15.00	.48950	177.3	24.53
16.00	.48236	176.2	15.06
17.00	.47552	162.8	11.81
17.50	.47213	165.5	11.70

The pressure correction was made by using the data previously employed by Hamer. We expressed the results at 25° so that comparison may be made directly with the measurements of previous investigators.<sup>6</sup>

**The Calculation of the Activity of Water in the Sulfuric Acid Solution.**—Since the activity of the water is required for subsequent calculations, it has been computed from our electromotive forces by two methods. The reaction of cells of Type I is



and the corresponding electromotive force is given by

$$E = E_0 + \frac{RT}{2F} \ln \gamma_{\text{H}}^2 \gamma_{\text{SO}_4} + \frac{RT}{2F} \ln m_{\text{H}}^2 m_{\text{SO}_4} - \frac{RT}{2F} \ln a_{\text{W}}^2 \quad (2)$$

where  $E$  is the electromotive force,  $E_0$  the molal electrode potential of the cell and the "m's" and "γ's" the molal concentrations and activity co-

(6) Brønsted, *Z. physik. Chem.*, **68**, 693 (1910); Lewis and Lacy, *THIS JOURNAL*, **36**, 804 (1914); Randall and Cushman, *ibid.*, **40**, 393 (1918); Ferguson and France, *ibid.*, **43**, 2150 (1921); Harned and Sturgis, *ibid.*, **47**, 945 (1925); Åkerlöf, *ibid.*, **48**, 1160 (1926); Trimble and Ebert, *ibid.*, **55**, 958 (1933); MacDougall and Blumer, *ibid.*, **55**, 2236 (1933).

efficients of the ionic and molecular species designated by the subscripts. The values of  $E_0$  which we have employed are those determined by Hamer.<sup>7</sup> To evaluate  $a_w$ ,  $\gamma^1$ , a preliminary activity coefficient, obtained by neglecting the term containing  $a_w$  was first computed. From these values of  $\gamma^1$ , a preliminary value of  $a_w$  may be computed by graphical integration of the general thermodynamic equation which relates the vapor pressure of the solvent with the activity coefficient of an electrolyte, namely

$$-\ln a_w = \ln \frac{p_0}{p} = \frac{m}{55.5} \left[ \nu + \frac{\nu}{m} \int_0^{\ln \gamma} m d \ln \gamma \right] \quad (3)^8$$

These values of  $a_w$  were then substituted in equation (2) and new values of  $\gamma^1$  were computed. This process was repeated until the values of  $\gamma$  and  $a_w$  satisfied this equation. This procedure was most convenient for concentrations below 0.1  $M$ . At higher concentrations a simpler method was adopted.

The electromotive forces of the cells of Type II are given by the equation

$$E' = E_0' - \frac{RT}{2F} \ln m_{\text{H}^+}^2 m_{\text{SO}_4} - \frac{RT}{2F} \ln \gamma_{\text{H}^+}^2 \gamma_{\text{SO}_4} \quad (4)$$

where  $E_0'$  is the molal electrode potential of the cell. Upon addition of equations (2) and (4), we obtain

$$E + E' - E_0 - E_0' = -\frac{RT}{2F} \ln a_w^2 \quad (5)$$

from which  $a_w$  may be computed easily. The values of  $E$  and  $E_0$  were taken from Hamer's data,  $E'$  from Table I, and  $E_0'$  from the values which we shall derive in a subsequent section. The values of  $a_w$  obtained by these are given at some of the temperatures in Table II. Values at intermediate temperatures may be interpolated.

TABLE II

THE ACTIVITY OF WATER IN SULFURIC ACID SOLUTIONS FROM 0 TO 60°

$m(\text{H}_2\text{SO}_4)$	0°	25°	40°	60°
0.0005	0.99998	0.99998	0.99998	0.99998
.01	.99959	.99960	.99961	.99962
.05	.99809	.99819	.99822	.99823
.1	.99620	.9964	.9964	.9964
.5	.9817	.9821	.9822	.9823
1	.9613	.9620	.9624	.9630
2	.9105	.9136	.9155	.9180
3	.8438	.8506	.8548	.8602
5	.6801	.6980	.7086	.7229
7	.5184	.5453	.5608	.5815

(7) Ref. 2, Table V, column (2).

(8) Harned, in Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Co., New York, 1931, Chap. XII, p. 779; Randall and Young, *THIS JOURNAL*, **50**, 989 (1928); Harned and Hecker, *ibid.*, **55**, 4838 (1933).

These results are in excellent agreement with the values from the direct vapor pressure measurements of Grollman and Frazer for dilute solutions at 25° and in more concentrated solutions with the data of Collins. The agreement with data of Brönsted is not so good. In Fig. 1 values of  $a_w$  at 0, 25 and 60° are plotted against  $m^{1/2}$ . The lines represent our data while other data which were obtained at 25° are represented by the symbols designated.<sup>9</sup>

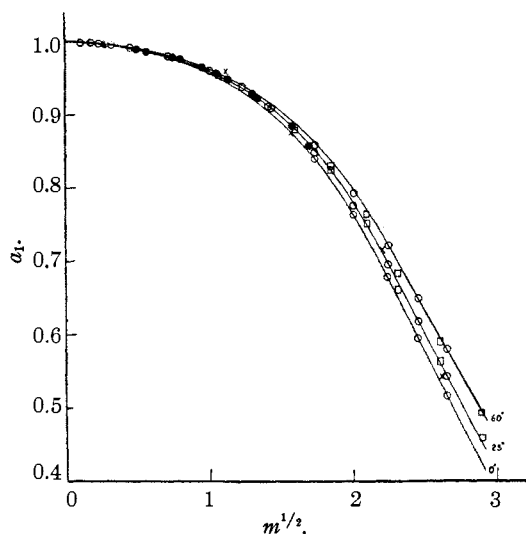


Fig. 1.—Water activity in sulfuric acid solutions from electromotive force and vapor pressure measurements: ●, Grollman and Frazer (25°); □, Collins (25°); ×, Brönsted (25°); ○, experimental.

For the purpose of computing activity coefficients of sulfuric acid in these solutions, we have computed the fourth term on the right of equation (2) which contains  $a_w$  from the data in Table I and the electromotive forces of cells of Type I. The result of this computation or the electromotive forces corrected for  $a_w$  elimination is given in Table III. For the sake of brevity, the results have been expressed by the equation

$$E = E_0'' + ct + dt^2 \quad (6)$$

Constants  $c$  and  $d$  were obtained by the method of least squares.  $E_0''$  is the electromotive force at 0°.

**The Activity Coefficient of Sulfuric Acid in Aqueous Solution from 0 to 60° and at Concentrations from 0 to 17.5  $M$ .**—Since cells of Type II cannot be extrapolated with any certainty, they were used for the computation of the activity coefficient at concentrations from 0.05 to

(9) Grollman and Frazer, *THIS JOURNAL*, **47**, 712 (1925); Collins *J. Phys. Chem.*, **37**, 1191 (1933); Brönsted, *Z. physik. Chem.*, **68**, 693 (1910).

TABLE III

THE ELECTROMOTIVE FORCES OF THE CELL  $\text{H}_2 \mid \text{H}_2\text{SO}_4(m) \mid \text{PbSO}_4 \mid \text{PbO}_2 \mid \text{Pt}$  AT ROUND CONCENTRATIONS AT  $0^\circ$ , CORRECTED FOR THE ACTIVITY OF WATER, AND CONSTANTS OF EQUATION (6)

$m(\text{H}_2\text{SO}_4)$	$E_0'$	$-c \times 10^6$	$d \times 10^8$
0.0005	1.42151	684.79	91.11
.0007	1.43276	659.06	90.28
.001	1.44458	636.80	92.22
.002	1.46706	603.96	90.28
.003	1.47976	588.96	90.77
.005	1.49528	581.72	89.94
.007	1.50502	574.54	91.11
.01	1.51540	566.82	92.06
.02	1.53427	536.35	91.27
.03	1.54464	514.16	90.63
.05	1.55733	488.53	90.50
.10	1.57398	465.65	88.12
.20	1.59038	423.92	86.96
.50	1.61231	356.34	86.00
1.00	1.63121	306.73	78.47
1.50	1.64429	274.53	75.12
2.00	1.65507	255.46	74.38
3.00	1.67536	247.94	72.92
4.00	1.69379	248.51	71.66
5.00	1.71096	254.19	70.42
5.00	1.72646	255.40	68.84
7.00	1.74061	260.37	67.78

17.5  $M$ . The activity coefficients derived from the cells of Type I agreed very closely with those computed from the results of the cells of Type II in the range of concentrations (0.05 to 7  $M$ ) in which both cells were measured if the values of  $a_w$  derived from vapor pressure measurements were employed.

In Table IV the values obtained by us at 0, 15, 25, 40 and  $60^\circ$  are compiled. From the results in Tables I and III and the equation

$$E = E_0 - \frac{3RT}{2F} \ln m \gamma^{4/3} \quad (7)$$

$\gamma$  was readily computed. The values of  $E_0$  of the cells of Type I employed were taken from Table IV, column (3) of the recent investigation of Hamer,<sup>2</sup> and the values of  $E_0$  for cells of Type II were those compiled in Table IV of the following section of this study. It is important to note that these molal electrode potentials were obtained by employing the Debye and Hückel theory.

The best agreement with other similar results previously reported is with the values of  $\gamma$  at the freezing point computed from freezing point measurements of Randall and Scott.<sup>10</sup> They obtained 0.912, 0.876, 0.825, 0.734, 0.648, 0.553, 0.424, 0.341 and 0.272 at the concentrations 0.0005, 0.001, 0.002, 0.005, 0.01, 0.02, 0.05, 0.1

(10) Randall and Scott, *THIS JOURNAL*, **49**, 647 (1927).

TABLE IV

THE STOICHIOMETRICAL ACTIVITY COEFFICIENT OF SULFURIC ACID IN AQUEOUS SOLUTIONS

$m$	$0^\circ$	$15^\circ$	$25^\circ$	$40^\circ$	$60^\circ$
0.0005	0.908	0.896	0.885	0.869	0.847
.001	.873	.848	.830	.806	.774
.002	.825	.783	.757	.722	.679
.005	.734	.674	.639	.593	.533
.01	.649	.582	.544	.495	.440
.02	.554	.489	.453	.407	.355
.05	.426	.371	.340	.301	.259
.1	.341	.293	.265	.227	.196
.2	.271	.231	.209	.181	.152
.5	.202	.171	.154	.133	.106
1	.173	.145	.130	.111	.0929
2	.170	.140	.124	.105	.0850
3	.201	.162	.141	.117	.0921
4	.254	.199	.171	.138	.105
6	.427	.318	.264	.205	.149
8	.686	.488	.397	.296	.205
10	1.012	.697	.553	.398	.266
12	1.431	.953	.743	.521	.337
14	1.958	1.264	.969	.664	.417
16	2.612	1.644	1.235	.828	.503
17.5	3.217	1.979	1.473	.972	.585
$E_0$ (Cell I)	1.6769	1.6816	1.6849	1.6923	1.6956
$E_0$ (Cell II)	0.63495	0.62307	0.61515	0.59900	0.58659

and 0.2  $M$ , respectively. It is apparent that the agreement is excellent. At  $25^\circ$  the values are much lower than those given by Lewis and Randall.<sup>11</sup> This is due principally to the fact that they employed in their calculation values of the relative partial molal heat content which were unquestionably too low. Our results are 2.4% higher than those obtained by Baumstark and those computed by Sherrill and Noyes.<sup>12</sup>

**The Molal Electrode Potential of the Mercury-Mercurous Sulfate Electrode.**—Since the electromotive forces of the cells of Type II were insufficiently accurate in dilute solutions for suitable extrapolation to zero acid concentration, we simply employed the values of  $\gamma$  derived from cells of Type I for the purpose of computing the molal electrode potential. The values of  $\gamma$  at 0.05, 0.07 and 0.1  $M$  were substituted in equation (4) as were also the values of  $E'$  obtained from the data in Table I, and  $E_0'$  was computed for each concentration. The mean value of the three determinations is given in Table V. They may be expressed to within approximately  $\pm 0.05$  mv. by the quadratic equation

$$E_0' = 0.63495 - 781.44 \times 10^{-6}t - 426.89 \times 10^{-9}t^2 \quad (8)$$

(11) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, pp. 354 and 356.

(12) Baumstark, Dissertation, Catholic University of America, Baltimore, Md., 1933; Sherrill and Noyes, *THIS JOURNAL*, **48**, 1861 (1926).

where  $E_0'$  is the normal potential of the cells. The constants of this equation were computed by the method of least squares.

TABLE V

THE MOLAL ELECTRODE POTENTIALS OF THE $\text{Hg}_2\text{SO}_4$   Hg ELECTRODE		THE $\text{SO}_4^{2-}$   Hg ELECTRODE	
$t$	$E_0$	$t$	$F_0$
0	0.63495	35	0.60701
5	.63097	40	.60305
10	.62704	45	.59900
15	.62307	50	.59487
20	.61930	55	.59051
25	.61515	60	.58659
30	.61107		

The result at 25° is 6 mv. lower than that computed by Lewis and Randall from the data of Randall and Cushman. It is also lower than the value calculated by Brodsky.<sup>13</sup> We are certain that our value is better since the activity coefficients of the acid computed from the electromotive forces of cells of Type II agree with similar ones computed from measurements of cells of Type I from 0.05 to 7 *M*. Secondly, our activity coefficients at 0° agree very well with those obtained from freezing point data of Randall and Scott. Finally we shall now proceed to show that our activity coefficients are consistent within narrow limits with the best heat data.

**The Relative Partial Molal Heat Content of Sulfuric Acid.**—From the electromotive forces of cells of Type I (Table II) after elimination of the term containing  $a_w$  or from those of cells of Type II, the partial molal heat content relative to a suitable concentration may be computed by the Gibbs-Helmholtz equation. We shall not describe the details of this well-known method of calculation but merely state the result. As reference concentration 0.05 *M* was chosen. The basis for the results in dilute solutions were the electromotive forces of cells of Type I. The results from 0.05 to 7 *M* were obtained from both cells of Types I and II and vapor pressure data, and those at higher concentrations from cells of Type II. For the purpose of brevity, we have expressed the results by the quadratic equation

$$(\bar{H} - \bar{H}_{0.05}) = (\bar{H} - \bar{H}_{0.05})_0 + \alpha t + \beta t^2 \quad (9)$$

where  $(\bar{H} - \bar{H}_{0.05})$  is the partial molal heat content relative to the 0.05 *M* solution at a temperature  $t$ ,  $(\bar{H} - \bar{H}_{0.05})_0$  is this quantity at 0° and  $\alpha$  and  $\beta$  are constants. The values of  $(\bar{H} - \bar{H}_{0.05})$ ,

(13) Lewis and Randall, "Thermodynamics," p. 407; Randall and Cushman, THIS JOURNAL, 40, 393 (1918); Brodsky, Z. Elektrochem., 35, 833 (1929).

$\alpha$  and  $\beta$  are given at concentrations from 0.0005 to 17.5 *M* in Table VI. It is to be remembered that  $(\bar{H} - \bar{H}_{0.05})$  was computed directly from observed electromotive forces from 0 to 60° at 5° intervals and that from these values the constants in the table were derived.

TABLE VI

THE RELATIVE PARTIAL MOLAL HEAT CONTENT OF SULFURIC ACID IN AQUEOUS SOLUTIONS AND CONSTANTS OF EQUATION (9)<sup>a,b</sup>

$m$	$(\bar{H} - \bar{H}_{0.05})_0$	$\alpha$	$\beta \times 10^3$	$\bar{L}_2(0)$
0.0005	-3795	+0.10	+1.20	397
.001	-3334	+ .45	+0.78	858
.002	-2711	- .09	+ .36	1481
.005	-1689	- .18	+ .48	2503
.01	- 948	+ .41	+ .73	3244
.02	- 461	+ .20	+ .85	3729
.05	0	0	0	4192
.1	480	+0.62	+0.64	4672
.2	711	.88	1.70	4903
.5	871	1.14	2.00	5063
1	1118	3.04	4.90	5310
2	1574	3.94	10.3	5766
3	2415	4.40	8.6	6607
4	3272	4.78	8.3	7464
6	4867	5.45	10.1	9059
8	6207	6.77	12.8	10399
10	7282	9.64	18.9	11474
12	8242	11.09	21.2	12434
14	9210	9.04	16.8	13402
16	10128	5.31	7.6	14320
17.5	10769	4.38	8.6	14961

<sup>a</sup> Values from 0.0005 to 0.05 *M* were obtained from the lead dioxide cells and the others from mercurous sulfate or lead dioxide cells. <sup>b</sup> Constants of equation (11):  $\alpha' = (\alpha + 7.128)$ ;  $\beta' = (\beta + 0.06628)$ .

Fortunately, comparison of these results may be made with values of  $(\bar{H} - \bar{H}_{0.05})$  computed from 0.0001 to 0.05 *M* from the calorimetric data of Lange, Monheim and Robinson.<sup>14</sup> In Fig. 2  $(\bar{H} - \bar{H}_{0.05})_{25}$  has been plotted against  $m^{1/2}$ . The circles represent our results and the dots the data of these investigators. The agreement is excellent since the maximum deviation is of the order of  $\pm 50$  cal. and most of the values agree within 20 cal. This confirms the accuracy of both the electromotive force and the calorimetric measurements.

In order to obtain  $\bar{L}_2$  or  $(\bar{H} - \bar{H}_0)$ , the relative partial molal heat content of the acid, we have employed the method which throughout is consistent with the theory of Debye and Hückel. To this end, we have evaluated  $\bar{L}_2$  by the equation

$$\bar{L}_2 = \nu RT^2 (\partial \ln \gamma / \partial T)$$

(14) Lange, Monheim and Robinson, THIS JOURNAL, 55, 4733 (1933).

Since 0.05  $M$  was chosen as reference concentration  $\bar{L}_2$  was computed at this concentration from 0 to 60° at 5° intervals. As previously noted ex-

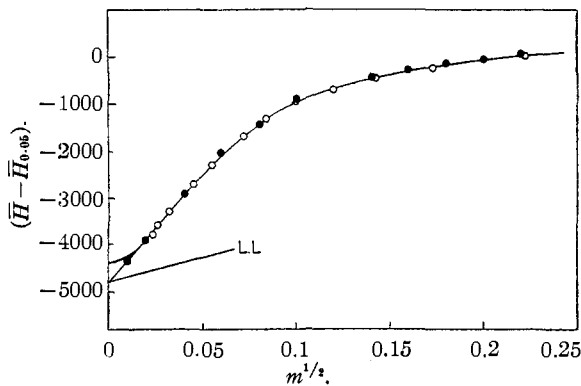


Fig. 2.— $(\bar{H}_{0.05} - \bar{H})_{25}$  vs.  $m^{1/2}$  in dilute solutions:  $\circ$ , e. m. f.;  $\bullet$ , Lange, Monheim and Robinson, calorimetric.

perimental results were obtained at all these temperatures. The temperature coefficients of  $\ln \gamma$  were obtained from a plot of  $\ln \gamma$  against  $T$ . The computed values were 4195, 4229, 4270, 4314, 4361, 4412, 4465, 4523, 4583, 4647, 4714, 4784 and 4857 cal./mole at 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55 and 60°, respectively.

These results may be expressed by the equation

$$(\bar{H}_{0.05} - \bar{H}_0) = \bar{L}_2 = 4192 + 7.128t + 0.06628t^2 \quad (10)$$

which was obtained by the method of least squares.

In Fig. 2 this extrapolation is represented by the curved line which is consistent with the limiting law of the theory of Debye and Hückel.

The limiting slope is reached in a region below 0.00001  $M$ . If we employ the purely empirical method of extrapolation of electromotive forces of Lewis and Linhart,<sup>2</sup> the result will be the straight line extrapolation which at no concentration approaches the requirement of theory. The difference between the two methods of extrapolation at 25° amounts to 460 cal.

Lange, Monheim and Robinson employed the straight line extrapolation and consequently their results agree with the Lewis and Linhart extrapolation. It is important to note that the extrapolation which is consistent with the Debye and Hückel theory is not inconsistent with their results except at 0.0001  $M$  where a discrepancy of the order of 50 cal. is found. This is not contradictory evidence, owing to the great difficulty of obtaining accurate experimental results in this region of concentration. In our opinion, the extrapolation in agreement with theory is required although no measurements of electromotive force or partial heats of dilution have been obtained at sufficiently low concentrations in sulfuric acid to prove the contention.

Upon addition of equations (9) and (10), we obtain

$$(\bar{H} - \bar{H}) = \bar{L}_2 = \bar{L}_{2(0)} + \alpha't + \beta't^2 \quad (11)$$

where  $\bar{L}_{2(0)}$  is the relative partial molal heat of dilution at 0° and at a given concentration and  $\alpha'$  and  $\beta'$  are the constants  $(\alpha + 7.128)$  and  $(\beta +$

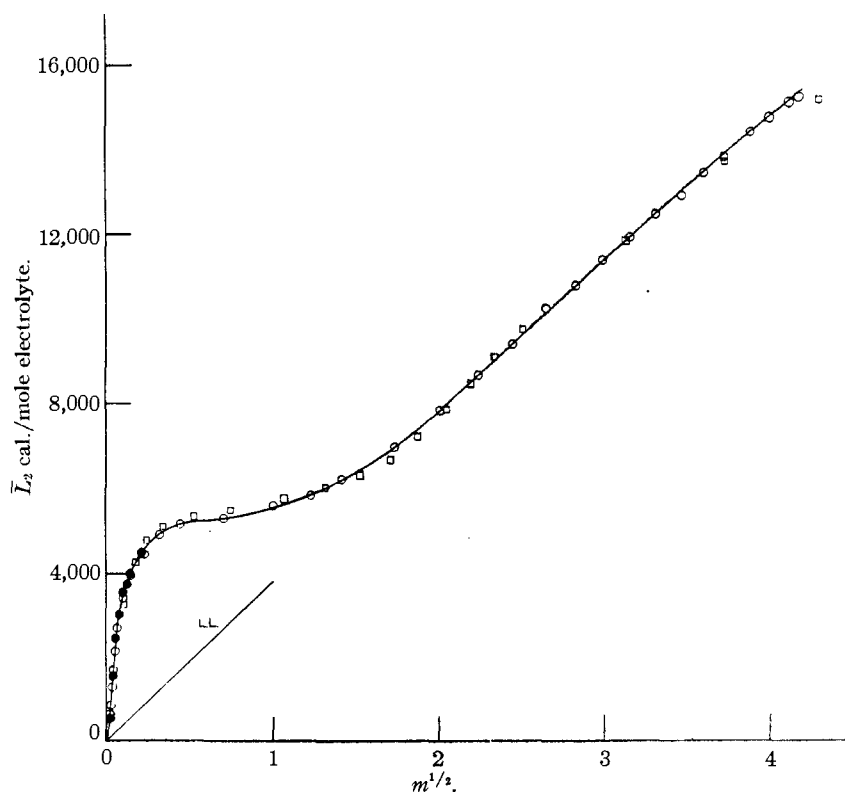


Fig. 3.— $\bar{L}_2$  vs.  $m^{1/2}$  from 0 to 17.5  $M$  at 25°:  $\circ$ , e. m. f.;  $\bullet$ , calorimetric;  $\square$ , e. m. f. (Brönsted).

0.06628), respectively. From the results in Table VI,  $\bar{L}_2$  at concentrations from 0 to 17.5  $M$  and 0 to 60° may be computed.

For further purposes of comparison,  $\bar{L}_2$  at 25° has been plotted against  $m^{1/2}$  over the entire concentration range in Fig. 3. The circles represent our results, the inked circles the results of Lange, Monheim and Robinson and the squares the values computed by Brönsted from electromotive force measurements. Since Brönsted's data were not determined in sufficiently dilute solutions for purposes of extrapolation, it was necessary to add 2530 cal. to each of his results. Our results and those of Brönsted<sup>15</sup> possess the same characteristics although the maximum deviation is of the order of 300 cal.

**The Relative Partial Molal Heat Capacity of Sulfuric Acid in Aqueous Solutions.**—By differentiation of equation (11) with respect to  $t$ , the relative partial molal heat capacity,  $\bar{C}_p - \bar{C}_{p0}$ , is readily obtained. Thus

$$(\bar{C}_p - \bar{C}_{p0}) = \frac{d\bar{L}_2}{dt} = \alpha' + 2\beta't = (\bar{C}_p - \bar{C}_{p0})_0 + 2\beta't \quad (12)$$

The constant  $\alpha'$  is seen to equal the relative partial molal heat capacity at zero degrees, and  $2\beta't$  gives the variation of this quantity with the temperature. Since these values involve the second differential coefficient of the original electromotive forces we cannot give too much weight to their accuracy.

(15) Brönsted, *Z. physik. Chem.*, **68**, 693 (1910); Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, p. 95.

### Summary

1. Measurements of the electromotive forces of the cells

$\text{H}_2 | \text{H}_2\text{SO}_4(m) | \text{Hg}_2\text{SO}_4 | \text{Hg}$  Type I  
from 0.05 to 17.5  $M$  and from 0 to 60° have been made.

2. From these and the cells

$\text{H}_2 | \text{H}_2\text{SO}_4(m) | \text{PbSO}_4 | \text{PbO}_2 | \text{Pt}$  Type II  
the activity of water in sulfuric acid solutions has been evaluated and found to be in good agreement with values computed from the best vapor pressure measurements.

3. From the combined results of these cells the activity coefficient of sulfuric acid from 0 to 60° and from 0.0005 to 17.5  $M$  have been calculated. In dilute solutions at 0°, the values obtained are in close agreement with the best freezing point data.

4. The normal potential of the mercurous sulfate-mercury electrode has been computed from 0 to 60°.

5. The relative partial molal heat content of sulfuric acid has been computed from 0 to 60° and from 0 to 17.5  $M$ . The results at 25° agree very closely with the best heat of dilution data.

6. The relative partial molal heat capacity of sulfuric acid and its variation with temperature has been estimated over the above temperature and concentration ranges.

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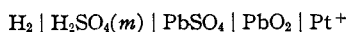
RECEIVED AUGUST 30, 1934

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

## The Molal Electrode Potentials and the Reversible Electromotive Forces of the Lead Accumulator from 0 to 60° Centigrade<sup>1</sup>

BY HERBERT S. HARNED AND WALTER J. HAMER

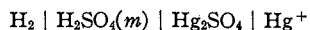
The present communication contains in a condensed and convenient form a summary of a very comprehensive study of the electrode potentials and reversible electromotive forces of the cells related to the lead accumulator. This will involve the employment of the measurements made by Hamer of the electromotive forces of the cells<sup>2</sup>



(1) This contribution is part of an investigation of the thermodynamic properties of the electrodes and electrolyte of the lead accumulator, and was aided by a grant from the Naval Research Laboratory, Anacostia Station, Washington, D. C., and is published with the permission of the Secretary of the Navy.

(2) Hamer, *THIS JOURNAL*, **57**, 9 (1935).

and of the cells



reported by Harned and Hamer.<sup>3</sup> The mercurous sulfate-mercury electrode was employed in place of the lead sulfate-two-phase lead amalgam electrode, since in solutions containing sulfuric acid the latter were found unrepeatable. Even though the greatest precautions were taken to eliminate air by the use of a vacuum technique, errors as high as 2 mv. occurred in the moderately dilute solutions.

To circumvent this difficulty, measurements of

(3) Harned and Hamer, *ibid.*, **57**, 27 (1935).