

mainly due to *conduction*, and therefore increases about in inverse proportion to the gap width. Gaps of from 1 cm. to 1.7 cm. according to circumstances, are best with ordinary calorimeters.

2. With large calorimeters, where the temperature change is less, freedom from detrimental convection is compatible with gap widths greater than those most desirable for small calorimeters.

3. In adiabatic work there is little fear of convection, hence either very large temperature intervals or very large air gaps can be profitably employed.

4. Very thin reflecting shields around the calorimeter may be used so as to diminish conduction, and thus decrease the total thermal leakage, without increasing convection.

5. Incidentally, it is pointed out that the ordinary rule, that thermometer lag causes no error where only one thermometer is used, deserves careful interpretation, or else re-statement, in the case of some thermochemical determinations.

WASHINGTON, D. C.

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

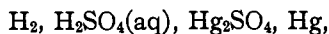
### THE FREE ENERGY OF DILUTION OF SULFURIC ACID.

BY MERLE RANDALL AND O. E. CUSHMAN.

Received November 16, 1917.

The number of accurate measurements from which the free energy of dilution of electrolytes involving bivalent ions may be calculated is limited. We have, at present, insufficient data, except in very dilute solutions, from which to calculate the degree of ionization or the activity of the ions of substances such as sulfuric acid. The occurrence of intermediate ions, such as  $\text{HSO}_4^-$ , which are probably present in considerable amount, and our inability to estimate their concentration, makes the problem of the interpretation of the result even less certain.

Lewis and Lacey<sup>1</sup> have studied the e. m. f. of the cell



at the two concentrations of sulfuric acid, 0.005 and 0.05 *M*. They found



Cells of this type have no liquid potential and the electromotive force determines the free energy of the reaction.<sup>2</sup>

Brönsted<sup>3</sup> has studied the above cell at various temperatures and over

<sup>1</sup> Lewis and Lacey, *THIS JOURNAL*, **36**, 804 (1914).

<sup>2</sup>  $\Delta F = -nEF$ . Lewis, *Ibid.*, **35**, 1 (1913).

<sup>3</sup> Brönsted, *Z. physik. Chem.*, **68**, 693 (1910).

a rather wide range of concentrations. His results will be discussed in a later section.

In this investigation the e. m. f. at  $25^{\circ}$  between hydrogen and mercurous sulfate electrodes in sulfuric acid at mol fractions 0.0009102 to 0.1288 has been determined.

**Hydrogen and Mercurous Sulfate Electrodes.**—The hydrogen electrodes were the same type as those described by Lewis and Rupert,<sup>1</sup> and by Lewis, Sebastian and Brighton.<sup>2</sup> The platinum electrode was covered with a thin layer of iridium black produced by depositing from a five per cent. solution of iridium sesquichloride. A very low current density was used and the direction of the current reversed for a few seconds every two minutes.

The hydrogen was produced in the electrolytic generator used by Lewis, Sebastian and Brighton. The sulfuric acid was prepared by diluting C. P. acid with conductivity water. The solutions at mol fraction 0.0009102 and 0.009014 were compared with 0.1 *M* and 1 *M* hydrochloric acid which was in turn standardized against silver chloride. Sulfuric acid of mol fraction 0.01824–0.1288 was standardized against fused sodium carbonate.<sup>3</sup>

The mercurous sulfate electrodes were of the usual form. They were prepared from pure mercury and from mercurous sulfate obtained by the method of Hulett.<sup>4</sup> These substances were shaken with the sulfuric acid, the solution decanted, and the process repeated several times as in the usual preparation of calomel electrodes. These electrodes were very constant in all the solutions used, and were reproducible to 0.0001 volt. If sulfuric acid is allowed to come in contact with the platinum lead wire the electrode is not constant or reproducible. The cell is therefore thoroughly dried, about 0.5 cc. of dry mercury added, and then the mixture of mercury, mercurous sulfate and sulfuric acid. Care is taken in stirring not to disturb the mercury at the bottom of the cell.

Three mercurous electrodes (Cells 1, 2 and 3) and the hydrogen electrode were dipped into a single intermediate vessel. The measurements are given in Table I. The first column gives the mol fraction of the sulfuric acid, the second, third and fourth columns give the e. m. f. measured against different sulfate electrodes, the fifth the barometric pressure, the sixth the mean value of each hydrogen electrode corrected for hydrogen at one atmosphere,<sup>5</sup> and the seventh the final mean. Each row represents

<sup>1</sup> Lewis and Rupert, *THIS JOURNAL*, **33**, 299 (1911).

<sup>2</sup> Lewis, Sebastian and Brighton, *Ibid.*, **39**, 2245 (1917).

<sup>3</sup> The carbonate method is the more accurate, and was used in those measurements made after the experiments with this method. Richards and Hoover, *THIS JOURNAL*, **37**, 95, 108 (1915); Randall and Scalione, *Met. Chem. Eng.*, **13**, 787 (1915).

<sup>4</sup> Hulett, *Phys. Rev.*, **32**, 257 (1911).

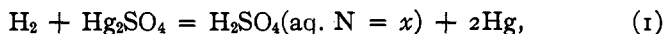
<sup>5</sup> Lewis, *THIS JOURNAL*, **35**, 1 (1913).

a new filling of the hydrogen electrode. The values for 0.005 *M* and 0.05 *M* acid obtained by Lewis and Lacey are given in the first two rows of the table.

TABLE I.  
E. M. F. of the Cell  $\text{H}_2, \text{H}_2\text{SO}_4, \text{Hg}_2\text{SO}_4, \text{Hg}$ .

Mol fraction. <i>N</i> .	E cell. 1.	E cell. 2.	E cell. 3.	Press. Cm.	E <sub>corr.</sub>	E <sub>mean.</sub>
0.00009009	..	..	..	..	..	0.8160
0.0008999	..	..	..	..	..	0.7545
0.0009102	0.7538	0.7540	..	75.7	0.7544	..
....	..	0.7541	0.7540	75.3	0.7545	..
....	..	0.7540	0.7539	75.8	0.7543	0.7544
0.009014	0.6956	0.6956	..	76.0	0.6960	..
....	0.6954	0.6954	..	75.3	0.6959	..
....	0.6953	0.6953	..	74.7	0.6960	..
....	0.6954	0.6954	0.6954	74.9	0.6960	..
....	0.6954	0.6954	..	75.3	0.6960	0.6960
0.01824	0.6745	0.6746	0.6746	75.5	0.6751	..
....	0.6744	0.6744	0.6744	74.8	0.6751	..
....	..	0.6743	0.6742	74.8	0.6750	0.6751
0.06149	0.6183	0.6182	0.6182	75.9	0.6187	..
....	0.6181	0.6183	0.6184	75.5	0.6186	0.6187
0.1288	0.5503	0.5502	0.5501	75.6	0.5506	0.5506

The values of the e. m. f. given in the table are the values obtained after the hydrogen had bubbled through the cell for several days and the value had become steady. In the case of the three most concentrated acids, the hydrogen, after leaving the cell, was bubbled through a small washing tube<sup>1</sup> containing a few cc. of 0.01 *M*  $\text{I}_2$  solution. In no case was there an appreciable change in the iodine concentration due to formation of  $\text{SO}_2$ . We may thus assume that the rate of reduction of sulfuric acid by hydrogen is too slow to affect our measurements. The free energy of the reaction



is given in the last column.

Edgar<sup>2</sup> has also measured this cell at several concentrations. His measurements were made at 25° in an apparatus similar to that used by the writers. The results are given in Table II and are marked E. Brönsted's<sup>3</sup>

<sup>1</sup> Cumming, *Trans. Faraday Soc.*, 6, 10 (1910).

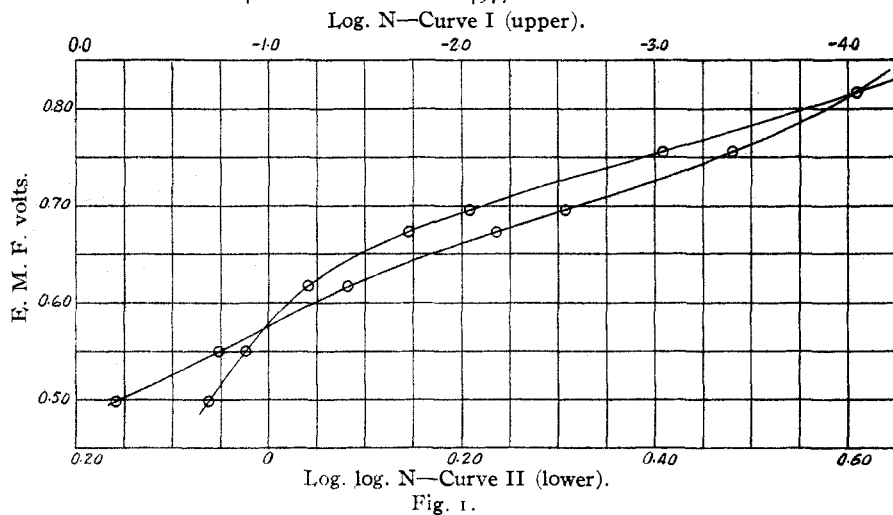
<sup>2</sup> See Lewis, Randall and Bichowsky, *THIS JOURNAL*, 40, 356 (1918).

<sup>3</sup> Brönsted, *Z. physik. Chem.*, 68, 693 (1910). From a study of Tables 18, 19 and 20 of Brönsted's paper it is evident that the values of  $\pi$  given in Table 18 for  $x = 0.02175$  are for a concentration  $x = 0.04255$ . In order to obtain a value for 25° at  $x = 0.02175$  the values of Table 20 were reduced to 1 atmos.  $\text{H}_2$  at the temperatures given and the value interpolated for 25°. The values given by Edgar (Thesis, Mass. Inst. Tech., Boston, 1912) were interpolated directly from Table 18 and corrected to 1 atmos.  $\text{H}_2$  at 25°. The correction of the results as given brings Brönsted's results into much better agreement among themselves and the corrected results agree quite closely with those of Edgar and of the present writers. These two corrected values are marked B<sup>2</sup> in the table.

measurements were made at various temperatures. They have been interpolated for 25° and calculated to H<sub>2</sub> at 1 atmos. The results are given under B in Table II.

TABLE II.

Mol. fraction <i>N</i> .	<i>E</i> .	Author.
0.0000868	0.8243	B
0.0002710	0.7927	B
0.0009555	0.749	E
0.001121	0.7493	B
0.004987	0.7144	B
0.008825	0.688	E
0.008946	0.694	E
0.02175	0.6674	B <sup>2</sup>
0.04255	0.6373	B <sup>2</sup>
0.08010	0.5989	B
0.1110	0.5676	B
0.2014	0.4977	B



In Fig. 1 the values of the e. m. f. given in Tables I and II are plotted as ordinates. The abscissas are log. mol fraction for curve I and log. log. mol fraction for curve II. The experimental results of Randall and Cushman and of Lewis and Lacey all fall upon the smooth curve.<sup>1</sup> The values of the e. m. f. of the cell H<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>(aq. *N* = *x*) Hg<sub>2</sub>SO<sub>4</sub>, Hg for round mol fractions<sup>2</sup> are given in the third column of Table III, and the corresponding value of the free energy  $\Delta F$  (Equation 1) in the fourth column.

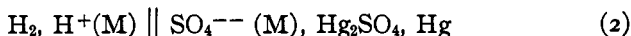
<sup>1</sup> The reliability of experimental data can often be inferred by plotting. In making interpolations or extrapolations it is important to choose the proper function of the variables. In Fig. 1, Curve I gives nearly a straight line for mol. fractions below 0.01 and Curve II for those above 0.05. In these regions the error of plotting is much reduced. The interpolated values of Table III were obtained by taking a mean of the interpolation by the aid of both functions. The error is not greater than 0.0002 volt.

<sup>2</sup> Intermediate values may be interpolated from the above table by assuming *E* or  $\Delta F$  proportional to log. *N*.

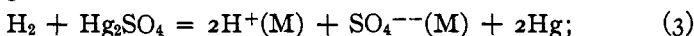
TABLE III.—FREE ENERGY OF THE REACTIONS  $H_2 + Hg_2SO_4 = H_2SO_4(N = X) + 2Hg$ ,  
 $2H^+ + SO_4^{--} = H_2SO_4(N = X)$ .

N.	Log N.	E.	$\Delta F$ (Eq. 1).	$\Delta F$ (Eq. 4).
0.00009009	-4.0453	0.8160	-37657	-9382
0.0008999	-3.0458	0.7546	-34822	-6547
0.002	-2.6990	0.7343	-33888	-5613
0.005	-2.3010	0.7114	-32830	-4555
0.01	-2.0000	0.6929	-31977	-3702
0.015	-1.8239	0.6812	-31437	-3162
0.02	-1.6990	0.6720	-31010	-2735
0.03	-1.5229	0.6571	-30323	-2048
0.04	-1.3979	0.6442	-29730	-1455
0.05	-1.3010	0.6315	-29140	-865
0.065	-1.1871	0.6145	-28360	-85
0.08	-1.0969	0.5975	-27573	702
0.10	-1.0000	0.5770	-26630	1645
0.13	-0.8861	0.5495	-25360	2915
0.20	-0.6990	0.4985	-23003	5272

Lewis and Lacey<sup>1</sup> from a consideration of the data in very dilute solutions found for the cell



corresponding to the reaction



$E^\circ = 0.6127$ ,  $\Delta F^\circ = -28275$  cal.

By subtracting Equation 1 from Equation 3 we obtain



These values of the free energy of formation from hypothetical molal hydrogen ion and sulfate ion are given in the last column of Table III.

Since the free energy of formation<sup>2</sup> of  $H^+$  is 0, the values in the last column also give the free energy of the reaction



The free energy of formation of sulfate ion from the elements has not as yet been determined.

BERKELEY, CAL.

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

## TOLANE CHLORIDES FROM CALCIUM CARBIDE, CHLORINE AND BENZENE.

By CLINTON DAVIDSON.

Received April 11, 1917.

**Preparation of  $\alpha$ -Tolane Dichloride.**<sup>3</sup>—If well-ground calcium carbide

<sup>1</sup> Lewis and Lacey, *THIS JOURNAL*, **36**, 804 (1914).

<sup>2</sup> Lewis and Randall, *Ibid.*, **36**, 1969 (1914).

<sup>3</sup> References on tolane dichlorides, *Ber.*, **4**, 289, 379 (1871); **12**, 1973 (1879); **15**, 900 (1882); **17**, 835 (1884); **29**, 2906 (1896); **40**, 2994 (1907).