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Researches on
The Physical Chemistry of the Lead-Acid
Storage Cell

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the

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The Potential of the Lead Dioxide-Lead Sulfate Electrode
at Various Temperatures

by

Walter J. Hamer and Herbert S. Harned

Due to the industrial importance of the lead dioxide-lead sulfate electrode, an accurate value of its potential is desired. Although extensive research has been done to determine this potential, the value is not known with precision. Gerke

Gerke, Chem.Reviews, 1, 390 (1925)

obtained 1.7 ± 0.1 v. at 25° from measurements of Kendrick.

Kendrick, Z.Electrochem., 7, 53 (1900)

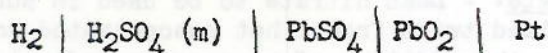
More recently, Vosburgh and Craig

Vosburgh and Craig, J. Am.Chem. Soc., 51, 2009 (1929)

obtained 1.681 ± 0.001 v. at 25° from measurements with a mercury-mercurous sulfate reference electrode. These values and others

Cumming, Trans.Faraday Soc., 2, 209 (1907)
Glasstone, J. Chem. Soc., 121, 1469 (1922)

show a diversity of ± 0.1 v. Part of this divergence is due to the use of various reference electrodes, the potentials of which are not well known and to the direct use of battery plates which may have been prepared in different methods and subjected to various treatments. In this contribution, measurements of the galvanic cell



will be employed to determine the potentials of the lead dioxide-lead sulfate electrode.

This cell also has additional interest as a means of determining the activities of aqueous sulfuric acid solutions. To this end measurements have been made over a concentration range of 0.0005 to 7.0 M and throughout a temperature range of from 0 to 60° .

Experimental Procedure.

Sulfuric Acid: - Dilute solutions of sulfuric acid were prepared from a high grade of sulfuric acid (sp.gr. = 1.8365) and conductivity water. This solution was analyzed gravimetrically and analysis was checked by titration with solutions of standard carbonate free sodium hydroxide. Phenolphthalein was employed as an indicator. The more concentrated solutions were prepared from sulfuric acid (sp.gr. = 1.8365) by weight and analysis was obtained by titration and from density determinations. These solutions were diluted to desired strength with conductivity water. The concentration of the solutions were known with an accuracy of $\pm 0.1\%$. The solutions were boiled in vacuo and kept under hydrogen until delivered into the cells. The stock solution was tested for sulfite and was found to be free of this impurity, hence distillation was not considered necessary.

Hydrogen: - Tank hydrogen purified by passing over copper heated to 700° was employed.

Hydrogen Electrodes: - Platinum foil electrodes were used. These were plated in a chloroplatinic acid solution for three minutes at a current density of 400 milliamperes. The electrodes were plated for a shorter time for very dilute solutions.

Cells and Bubble Tubes: - The apparatus described by Hamer

Hamer, J. Am. Chem. Soc., 56, 860 (1934)

was employed for these measurements. In this case the three way stopcock was essential to prevent hydrogen from coming into contact with the lead dioxide. Although lead dioxide is reduced only at temperatures above 140° in the vapor phase, its reduction may take place at much lower temperatures in solution

Wright and Luff, J. Chem. Soc., 33, 532 (1878)

Potentiometer: - Type K, Leeds and Northrup potentiometer was employed. Measurements of voltages above 1.6 v. were made by the method suggested in the Leeds and Northrup pamphlet.

Lead Nitrate: - Lead nitrate to be used in subsequent preparations was recrystallized twice from a hot concentrated solution of high grade lead nitrate by the addition of a concentrated solution of nitric acid. In the second precipitation redistilled nitric acid was employed.

Lead Sulfate: - 500 cc. of 0.5 M lead nitrate and 500 cc. of 0.5 M sulfuric acid were added drop by drop to 2 liters of boiling 0.1 M sulfuric acid. The solution was constantly stirred by a current of dry carbonate free air during the precipitation. The lead sulfate was well washed and digested 24 hours on a steam bath under 2 M sulfuric acid. The final preparation was kept under 0.1% sulfuric acid until used.

Lead Dioxide: - (1) Dilute lead nitrate solution was added drop by drop to a dilute solution of sodium hydroxide. The lead hydroxide formed was well washed and then dissolved by means of sodium hydroxide. The resulting sodium plumbite solution was heated to 93°, and while mechanically stirred bromine was added slowly until the precipitate turned dark brown.

(2) This preparation was the same as No. 1 except that a stream of chlorine gas was bubbled into the sodium plumbite solution instead of bromine. The chlorine was generated by the action of concentrated hydrochloric acid on potassium permanganate and was washed by bubbling through water.

(3) This sample was prepared by the oxidation of sodium plumbite solution with hydrogen peroxide.

(4) 100 grams of lead nitrate and 400 cc. of concentrated nitric acid in a total volume of 3 liters was electrolyzed at 93°. The anode was a platinum gauze and the cathode a platinum wire sealed into glass and surrounded by a porous cup. The current density was maintained at 2.5 amperes per square centimeter and a current of dry carbonate free air was used to stir the solution.

(5) A small quantity of electrolytically prepared lead dioxide was dissolved with hot concentrated carbonate free sodium hydroxide solution under an atmosphere of nitrogen. The solution was filtered and added drop by drop to a large volume of conductivity water kept at 93° and constantly stirred.

(6) This sample was the same as No. 5 except that precipitated lead dioxide (No. 1) was used in place of electrolytically prepared lead dioxide.

(7) Two different samples of commercial lead dioxide were digested two weeks with 3 M sulfuric acid, filtered, and redigested for several days. A small portion of each was treated by method No. 5 before digesting.

Digestion of Lead Dioxide: - All of the above preparations were digested separately under 3 M sulfuric acid on a steam plate for a week. This digestion brings the dioxide into a more stable state

Vosburgh and Craig, J. Am.Chem.Soc., 51, 2009 (1929), p.2011.

and also converts any monoxide into lead sulfate. Since lead sulfate is added later its formation is not undesirable. Preparations which preclude this digestion were not employed. They were found to be unsatisfactory by Vosburgh and Craig

Vosburgh and Craig, J. Am.Chem.Soc., 51, 2009 (1929), p.2012
See also Glasstone, J. Chem. Soc., 121, 1469 (1922)

lead dioxide was kept under 0.1% sulfuric acid until used.

Lead Dioxide-Lead Sulfate Electrodes:- Lead dioxide was quickly sucked dry in a Gooch crucible, the bottom of which was covered with filter paper. It was then transferred to a glass stoppered flask containing sulfuric acid of concentration to be used in the cell. Lead sulfate dried in like manner was then added and the flask was shaken from 15 to 30 minutes. This paste was then placed in the cell compartment over a sealed in platinum wire and sulfuric acid was introduced into the evacuated cell. The relative amounts of lead dioxide and lead sulfate could be varied but it is better to have approximately the same amounts of each. Unsatisfactory results are obtained if only traces of either are used.

Preliminary Measurements

Preliminary measurements were made with each of the lead dioxide preparations to determine which was the most stable and which gave the most consistent and reproducible results. All electrodes were constructed as described above. In Table 1 the electromotive forces are given at 25° for the various preparations of lead dioxide after equilibrium had been reached. Two series are given for each kind at the same concentration. All these measurements were made with boiled solutions and the cells were filled in vacuo. All samples came to equilibrium within two hours except at 0° where from three to four hours were required. After equilibrium has been reached at one temperature a much shorter time is required for equilibrium with change of temperature.

A study of Table I shows that preparations (4), (5), and (6) are the most desirable and gave measurements consistent to within ± 0.1 mv. The commercial samples evidently could not be sufficiently purified. The low results obtained by the first two methods are probably due to the tenacity of lead dioxide to occlude the impurities, sodium bromide and chloride, which are formed in their preparation and which resist all effort of removal. The third preparation probably gives low results for the same reason or due to a possible colloidal condition. All the methods give amorphous lead dioxide except No. 4 which gives a fine preparation of crystalline lead dioxide. Cumming

Cumming, Trans. Faraday Soc., 2, 209 (1907)

and Glasstone

Glasstone, J. Chem. Soc., 121, 1469 (1922)

found that crystalline lead dioxide gives a higher potential than the amorphous variety. The results of (5) and (6) indicate that this is true but that the differences amount to only a few tenths of a millivolt, and that the low values of (1), (2), and (3) are due to other additional effects.

Lead dioxide prepared by electrolysis gave the most consistent results and were reproducible to better than ± 0.1 mv. Consequently, all subsequent measurements were made with it. The preparations (5) and (6) may also be used, but their preparations are slow and only small quantities are obtained.

Electromotive Forces of the Cells $\text{H}_2 \mid \text{H}_2\text{SO}_4 (m) \mid \text{PbSO}_4 \mid \text{PbO}_2 \mid \text{Pt}$

Three series of measurements were made. In series A, new lead dioxide-lead sulfate electrodes were prepared for each run from a new supply of the mixed paste. In series B, the paste was kept after each run, re-treated and then re-used. In series C, a new electrolytic preparation of lead dioxide was employed and the procedure of series B was followed. The three series checked well and a paste of lead dioxide-lead sulfate can be repeatedly used with good results. In fact this procedure is to be recommended since an electrode of constant composition is used for all measurements. These measurements were made at five degree temperature intervals from 0 to 60°. All electromotive forces were corrected to one atmosphere hydrogen pressure employing the combined vapor pressures of aqueous sulfuric acid of Grollman and Frazer,

Grollman and Frazer, J. Am. Chem. Soc., 47, 712 (1925)

Brönsted,

Brönsted, Z. physik. Chem., 68, 693 (1910)

and Collins.

Collins, J. phys. Chem., 37, 1191 (1933)

The corrections for 0° were obtained by extrapolation of above data. For dilute solutions the vapor pressures of pure water may be employed. For the sake of brevity the electromotive forces were least squared using the equation

$$E = E_0 + at + bt^2 \quad (1)$$

where t is temperature in degrees Centigrade, a and b are constants and E_0 is the electromotive force at 0°. The values of E_0 , a and b are given in Table 11. The molalities are given in column 1 of the same table. All electromotive forces are the average of duplicate cells.

Values of the electromotive forces at round concentrations were desired. These were obtained from a large plot of $E - RT/2F \ln m_{\text{H}^+} m_{\text{SO}_4}^2$ against $m_{\text{H}^+} / 4^{1/3}$. At concentrations below 0.01 M it is necessary to

correct for the solubility of lead sulfate in sulfuric acid. The molalities of the sulfate-ion at 20, 25 and 30° due to this solubility were taken from the average values obtained by graphical interpolation of solubility measurements made by Pleissner

Pleissner, Arb. Kaiser Ges. Amt., 26, 419 (1907)

at 18°, by Huybrechts and Ramelot

Huybrechts and Ramelot, Bull. soc. chim. Belg., 36, 239 (1927)

at 18 and 30°, and by Purdum and Rutherford

Purdum and Rutherford, J. Am. Chem. Soc., 55, 3221 (1933)

at 20°. The solubility of lead sulfate in water

Böttger, Z. physik. Chem., 46, 604 (1903)

Kohlrausch, Z. physik. Chem., 64, 129 (1908)

Huybrechts and de Langeron, Bull. soc. chim. Belg., 39, 43 (1930)

was also employed in this graphical interpolation and extrapolation. To obtain the molalities of the sulfate-ion at other temperatures the above values were plotted against $1/T$ and the best straight line was drawn and extrapolated to 0 and 60°. Values obtained in this manner are given in Table III. In the third and fourth columns of this table the values of r and s for the equation $S = S_0 + rt + st^2$ are given, where S and S_0 represent the solubility of lead sulfate in sulfuric acid at temperatures t and 0° respectively. The constants r and s were obtained by the graphical method of Harned and Nims

Harned and Nims, J. Am. Chem. Soc., 54, 423 (1932)

Table III.

Solubility of Lead Sulfate in Sulfuric Acid from 0 to 60°^{oa}.

$M(H_2SO_4)$	$S_0 \times 10^{-6}$	$r \times 10^{-8}$	$s \times 10^{-10}$
0.0004	34.0	80.6	3.0
.0005	32.3	76.0	2.5
.0007	28.5	66.6	2.2
.001	23.0	60.0	2.0
.002	16.0	40.0	1.6
.003	11.0	25.0	1.4
.005	9.0	20.0	1.0
.007	8.0	10.0	0.7
.01	7.0	5.0	0.5

a_ These values are expressed in moles per 1000 grams of water. These values were incorporated in the smoothing process by calculating the change in the potentials produced by the increase in the sulfate-ion concentration or more simply by substituting the total sulfate-ion concentration in the formula given above for smoothing. Dolezalek and Finckli

Dolezalek and Finckli, Z. anorg., 51, 323 (1906)

and Glasstone

Glasstone, J. Chem. Soc., 121, 1469 (1922) gives the solubility product of $(\text{Pb})(\text{OH})_4$ as 3.25×10^{-66}

found the solubility of lead dioxide in sulfuric acid to be extremely small in dilute solutions and no corrections for its solubility were necessary.

The values of the electromotive forces read from the curve at round concentrations were expressed by the equation

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

and the constants c and d were obtained by the method of least squares. The values of the electromotive forces at 0° and of c and d are given in Table IV. This procedure is usually adopted in the calculation of thermodynamic data from electromotive force measurements in order to distribute the experimental error more evenly.

Evaluation of the Normal Electrode Potential, E_0 , of the Lead Dioxide-Lead Sulfate Electrode: - The chemical reaction represented by the galvanic cell is



and the electromotive force is given by the equation

$$E = E_0 + (RT/2F) \ln m_{\text{H}}^2 m_{\text{SO}_4} + (RT/2F) \ln \gamma_{\text{H}}^2 \gamma_{\text{SO}_4} - (RT/2F) \ln a_{\text{H}_2\text{O}}^2 \quad (3)$$

where E is the measured electromotive force of the cell at a molal concentration, m, E_0 is the normal electrode potential of the lead dioxide-lead sulfate electrode, and "m's" and "γ's" represent molalities and activity coefficients, respectively, of the ionic species denoted by subscripts.

We shall first treat sulfuric acid as a completely dissociated electrolyte and employ stoichiometrical molalities in our extrapolations. Equation (3) may be rearranged in the form

$$E - (RT/2F) \ln m_H^2 m_{SO_4} = E_0 + (RT/2F) \ln \gamma_H^2 \gamma_{SO_4} - (RT/2F) \ln a_w^2 \quad (4)$$

and if the left side is plotted against the square root of the molality a straight line should be obtained in dilute solution range and the extrapolation at zero concentration gives E_0 since by definition the last two terms on the right vanish. A straight line is obtained for this function for completely dissociated electrolytes, but little is known for this function for incompletely dissociated electrolytes. This is the method suggested by Lewis and Linhart

Lewis and Randall, "Thermodynamics", McGraw-Hill Book Company, Inc., New York, p. 334.

and accurate data in dilute solutions are needed for its successful application. As an aid in the extrapolation the activity coefficients of Randall and Scott

Randall and Scott, J. Am. Chem. Soc., 49, 647 (1927)

at 0° calculated from freezing point determinations were used to evaluate the second term on the right of equation (4). The differences between this term and the left side of same equation gives E_0 , when a_w a very small term is neglected. The electromotive force measurements were drawn parallel to their curve as suggested by Randall and Young

Randall and Young, J. Am. Chem. Soc., 50, 989 (1928)

The extrapolations of the left side of equation (4) against $m^{1/2}$ are given in Fig. 1 at $0, 25, 45$ and 60° from 0.0005 to 0.01 M. The lower curve is the one given by freezing point measurements. For clear comparison with electromotive force measurements 0.002 v. has been subtracted from these measurements. The freezing point curve has a slight "hump" below 0.002 M but may be due to the arbitrary extrapolation by Randall and Scott of their "j" function in dilute solutions. Our points are not accurate enough to justify this slight "hump" and we have drawn our line straight. The same was done at the other temperatures. The E_0 's determined in this manner are given in the second column of Table V. These were least squared to fit a quadratic equation, and the equation with numerical values is

$$E_0 = 1.6769_4 + 342.17 \times 10^{-6}t + 83.11 \times 10^{-8}t^2 \quad (5)$$

Values of E_0 calculated by this equation are given in the fourth column of Table V.

Evaluation of the Normal Electrode Potential, E_0 , of the Lead Dioxide-Lead Sulfate Electrode by a Method Employing the Ionization Constant of the Bisulfate Ion, K_2 : - In the above method for extrapolation we have employed stoichiometrical concentrations. Sulfuric acid is known to be a moderately strong electrolyte, the second step in its ionization being incomplete. This is qualitatively shown to be true in Fig. 1. The straight lines labeled "L.L." are those predicted from the limiting law of Debye and Hückel for a completely dissociated electrolyte. The experimental slopes are greater and below the theoretical which indicates ionic association, and that the association increases with temperature. Recently, Hamer

Hamer, J. Am. Chem. Soc., 56, 860 (1934)

determined the ionization constants of the bisulfate ion from 0 to 60° from measurements of galvanic cells, and confirmed this phenomena of increased association with increase in temperature.

If the value of the hydrogen ion given by the equation

$$K_2 = (m_{\text{H}^+} m_{\text{SO}_4} \gamma_{\text{H}^+} \gamma_{\text{SO}_4}) / (m_{\text{HSO}_4} \gamma_{\text{HSO}_4}) \quad (6)$$

is substituted in equation (3), the equation

$$E = E_0 + (RT/2F) \ln m_{\text{H}^+} m_{\text{HSO}_4} + (RT/2F) \ln \gamma_{\text{H}^+} \gamma_{\text{HSO}_4} + (RT/2F) \ln (K_2 / a_w^2) \quad (7)$$

results. It is to be noticed that although this equation appears to express sulfuric acid as if it were un-univalent it really expresses it as an electrolyte with a varying γ value since real ionic concentrations are involved. If the limiting law of Debye and Hückel with an additional term proportional to the ionic parameter is employed to express the third member on the right of equation (7) the equation

$$E - (RT/2F) \ln m_{\text{H}^+} m_{\text{HSO}_4} + 2 A \mu'^{1/2} - (RT/2F) \ln K_2 = E - (RT/2F) \ln \left(\frac{a_w^2}{\beta \mu'} \right) \quad (8)$$

results. Since all quantities on the left side may be either obtained experimentally or evaluated, an extrapolation of the left side against μ' gives E_0 at zero concentration, since the second term on the right side vanishes by reason of its definition. The slope of the curve gives the value of β which may or may not be constant with μ' . Equation (8) is equivalent to the equation

$$E - (RT/2F) \ln m_{\text{H}^+}^2 m_{\text{SO}_4} + 6 A \mu'^{1/2} = E_0 - (RT/2F) \ln a_w + \beta \mu' \quad (9)$$

which is derivable from equation (3) and the limiting law of Debye and Hückel with an additional term proportional to the ionic parameter. This equation is similar to the one employed by Hitchcock

Hitchcock, J. Am. Chem. Soc., 54, 1350 (1932)

for univalent electrolytes. In this case the equation cannot be used satisfactorily for extrapolation since we have an unsymmetrical valence type and an incompletely dissociated electrolyte. Equation (9) gives a very sharp curve below 0.01 M when plotted against the ionic strength. It is equivalent to equation (8) only when real ionic concentrations are used. When these are substituted in equation (8) or (9) and the left side of either is plotted against the corresponding real ionic strength an extrapolation is possible. Only a slight curve is obtained.

The ionic concentrations of each of the ions, H^+ , HSO_4^- and SO_4^{2-} were obtained from the equation (6) and the logarithm of the activity coefficient ratio was obtained from the limiting law of Debye and Huckel. In equation (6) $m_H = M + m_H'$, $m_{SO_4} = m_H'$ and $m_{HSO_4} = M - m_H'$ where M is the stoichiometrical concentration and m_H' is the concentration of the sulfate or hydrogen ion produced in the ionization of the bisulfate ion. The ionic strength is equal to $M + 2 m_H'$. The values of m_H' and the ionic strength were obtained by successive approximations. In these calculations, the values of K_2 obtained by Hamer

Hamer, J. Am. Chem. Soc., 56, 860 (1934)

These values did not fit the parabolic relation given by Harned and Embree, J. Am. Chem. Soc., 56, 1050 (1934) in which they employed a universal constant of 0.00005. Sulfuric acid however does fit a parabolic equation with a constant of 0.00008 and is expressed by $\log K_2 = 8.1756 - 10 - 0.00008 (t + 9.1)^2$ where -9.1° is the temperature of the maximum within the experimental error of one percent. Since this is true and the parabolic function is so sensitive, the experimental values were employed.

were employed and the A values are taken from column 2 of Table VII at various temperatures of the paper of Harned and Ehlers

Harned and Ehlers, J. Am. Chem. Soc., 55, 2179 (1933)

The values of the ionic concentrations of each of the three ions, the ionic strength, and the activity coefficient ratio of equation (6) are given in Table VI at the stoichiometric molalities given in the first column. These quantities are in reality only "apparent" since the extended term of Debye and Hückel

or the extended terms of LaMer, Gronwall and Grieff

LaMer, Gronwall and Grieff, J. Phys. Chem., 35, 2245 (1931)

for unsymmetrical valence type electrolytes have not been employed. These corrections were not introduced because no knowledge of the ionic parameter is at hand and there is some doubt of the application of the extended theory to incompletely dissociated electrolytes. It is likely that the ionic parameter changes rapidly with concentration. However, the concentrations should become more nearly the true value and less "apparent" as dilution progresses and since the extrapolated value is of immediate concern, we have not added this refinement.

The second term on the left of equation (8) or (9) was calculated from the data of Table VI and the left side of this equation was plotted against the corresponding ionic strength given in Table VI. These extrapolations are given at 0, 25, 45 and 60° in Fig. 2. It will be noticed that a straight line with little or no slope is obtained at higher temperatures and that only a slight curve is obtained at lower temperatures. This is a gratifying conclusion in that the β value is nearly zero and its omission in the successive approximation produces but little error and gives ionic concentrations fairly accurate in dilute solutions. At zero degrees the Hitchcock extrapolation using equation (9) and stoichiometric concentrations is given. It is evident that this function is unsuited for this electrolyte. The extrapolated values are given in the third column of Table V and the least squared values in the fifth column of same table. The latter were calculated from the equation

$$E_o = 1.6769_4 + 291.9 \times 10^{-6} t + 108.77 \times 10^{-8} t^2 \quad (10)$$

The two methods must give the same extrapolated values since the electrolyte becomes more completely dissociated with dilution and the total concentration of hydrogen ion calculated from equation (6) must approach the completely dissociated value, or $M + m_H' = 2M$ or $m_H' = M$. The values are not exactly equal, the divergence increasing with temperature until the two differ by 2 mv. at 60° with the latter method giving the lower value. This divergence is not due to an error in K_2 as the second and third terms in equations (8) and (9) have a counteracting action on each other and the use of K_2 is merely employed to give a satisfactory extrapolation. It must be pointed out here that method 11 involves the limiting law of Debye and Hückel which necessarily assumes that the activity coefficient must approach the limiting law at some conceivable concentration. However, as the curves were drawn in Fig. 1 this is not true and for the two methods to check the curves must bend below 0.0005 M which cannot be detected experimentally. This would seem to indicate that the "hump", even though slight, found from

Randall and Scott's data at 0° were real and that a similar "hump" should be observed at higher temperatures and that it would be more marked as the temperature is raised. We believe that the second method is a more powerful method of extrapolation and that the E_0 values obtained by this method are more reasonable. In Fig. 1 the dotted lines correspond to this "hump". Of course, various extended terms may influence the second method of extrapolation, or a finite value for the ionization of the first step may account for this divergence. However, these should extrapolate out to a large extent, and lead to a correct E_0 value.

Activity of Water in Sulfuric Acid Obtained by Two Methods and the Stoichiometrical Activity Coefficients of Sulfuric Acid Calculated from the E_0 Values Obtained by the First Method: - Before activity coefficients can be calculated from the E_0 's and the electromotive forces, the latter must be corrected for the term involving the activity of water. These corrections were obtained by first calculating γ' a quantity which contains the water term and which as a consequence is too high. These quantities were used in the method of Randall and Young

Randall and Young, J. Am. Chem. Soc., 50, 989 (1928)

and the activity of water was calculated by the evaluation of the area. These values were used in a new calculation of γ and the process was repeated until the two quantities γ and a_w were consistent. This procedure was employed for electromotive forces below 0.1 M and the corrections in the electromotive forces amounted to 0.1 mv. and less. For molalities above 0.1 M the activity of water was obtained by a more convenient and more accurate method. In the following contribution measurements of the galvanic cell $H_2 | H_2SO_4(m) | Hg_2SO_4 | Hg$ will be given. The electromotive force of this cell is given by

$$E' = E_0' - (RT/2F) \ln m_H^2 m_{SO_4} \gamma_H^2 \gamma_{SO_4} \quad (11)$$

and if this expression is added to equation (3) we obtain

$$E + E' - E_0 - E_0' = - (RT/2F) \ln a_{H_2O}^2 \quad (12)$$

The activity of water calculated from this equation was used to correct the electromotive forces given in Table IV. The manner in which E_0' was obtained will be presented in the paper to follow. The values of the activity of water from 0 to 60° are given in Table VII. They are in excellent check with the values of Grollman and Frazer

Grollman and Frazer, J. Am. Chem. Soc., 47, 712 (1925)

for dilute solutions at 25° and with Collins

Collins, J. Phys. Chem., 37, 1191 (1933)

at 25° and for the more concentrated solutions. The values of Brønsted

Brønsted, Z. physik. Chem., 68, 693 (1910)

fit only fairly well. The check is only fair at other temperatures with the available data. In Fig.2 they are plotted against $m^{1/2}$ at 0, 25, and 60°.

The activity coefficients from 0 to 60° are given in Table VIII and it will be noticed that they decrease very rapidly with temperature. The values at 0° are in excellent check with those of Randall and Scott except at the lowest concentrations where the "hump" occurs. The values at 25° are much lower than those given by Lewis and Randall

Lewis and Randall, "Thermodynamics", McGraw-Hill Book Company, Inc., New York, 1923, pages 354 and 356.

which were calculated assuming low partial molal heat contents. They are, however, in closer check with the unpublished values of Baumstark

Baumstark, Dissertation, Catholic University of America, Baltimore, Md., 1933

and those calculated by Sherrill and Noyes

Sherrill and Noyes, J. Am. Chem. Soc., 48, 1861 (1926)

Stoichiometrical Activity Coefficients of Sulfuric Acid Solutions
Calculated from the E_0 Values Obtained by the Second Method: - The activity coefficients calculated employing the electromotive forces given in Table IV, the activity of water of Table VII and the E_0 values given in column 3 of Table V are given in Table IX. These may be obtained directly by adding $\Delta / (3RT/2F)$ to the logarithm of γ given in Table VIII. Δ is the difference in columns 4 and 5 of Table V and are given in the sixth column of Table V. In these calculations the curve corresponding to the "hump" was employed. For this to be true, the electromotive forces given in second column of Table IV above 0.001 M remain the same. For 0.0005 and 0.0007 M we add 0.15 mv.

and for 0.001 M we add 0.13 mv. which certainly does not clearly define a "hump". The values at 0° are of course in better with the freezing point data of Randall and Scott

Randall and Scott, J. Am. Chem.Soc., 49, 647 (1927)

since our curve was drawn exactly parallel to theirs. The values at other temperatures are much higher than those obtained by the first method and are more reasonable. The values are still lower at 25° than those given by Lewis and Randall

Lewis and Randall, "Thermodynamics", McGraw-Hill Book Company, Inc., New York, 1923, pages 354 and 356.

but are in excellent check with those predicted by Sherrill and Noyes

Sherrill and Noyes, J. Am. Chem. Soc., 48, 1861 (1926)

They calculated a value of 0.269 for 0.1 M from their second ionization constant and ionic activities. Our value of 0.266 is surprisingly close. Incidentally, Baumstark gives 0.276 for this concentration.

Real Activity Coefficients of Sulfuric Acid Solutions: - In the above we have calculated stoichiometrical activity coefficients. Activity coefficients at the real ionic strength may be calculated from the data of Tables VI and VIII, since $m_{\pm} \gamma_{\pm} = m_{\pm}' \gamma_{\pm}'$. However, corresponding ionic strengths must be used in place of mean molalities, since an interpretation of the meaning to be attached to the latter is obscure. The primed quantities refer to the real ionic values and the unprimed to stoichiometrical. These calculations are not incorporated in the present contribution since in reality they give only "apparent" real activity coefficients due to the "apparent" nature of the values given in Table VI. Suffice it to say that these values should be higher than the former stoichiometrical values and that the two series approach each other with dilution due to increased dissociation. For practical purposes, the stoichiometrical values are sufficient as the properties of sulfuric acid can easily be defined in terms of molality and the corresponding activities.

Summary.

- (1) A study of the lead dioxide-lead sulfate electrode has been made. Crystalline lead dioxide prepared by electrolysis gave the most consistent results and were reproducible to within ± 0.1 mv.

- (2) Crystalline lead dioxide gives higher potentials than amorphous.
- (3) Measurements of the galvanic cell $H_2 | H_2SO_4(m) | PbSO_4 | PbO_2 | Pt +$ have been made over a concentration range of 0.0005 to 7.0 M and throughout a temperature range of from 0 to 60°.
- (4) Values of the normal electrode potential of the lead dioxide-lead sulfate electrode have been determined from 0 to 60°, and a discussion is given of the probable form of the extrapolation function based upon two methods of extrapolation, one of which employs the ionization constants of the bisulfate ion of Hamer.
- (5) Activity coefficients of sulfuric acid have been determined. These are the stoichiometrical values. Factors involved in the evaluation of the real quantities are discussed.
- (6) Activity of water in sulfuric acid has been calculated.

Table 1

Comparisons of the Electromotive Forces of Various Lead Dioxide

Preparations at 25° Centigrade.^a

PbO ₂ Prep. ^b	0.01945 M	0.04945 M	0.09798 M	0.9967 M
1	1.51937 v 1.51952	1.54391 v -----	1.56133 v 1.56092	1.6228g -----
2	1.51984 1.51963	1.54452 1.54471	1.56127 1.56163	----- -----
3	1.51997 1.51948	1.54400 -----	1.56177 1.56151	----- -----
4	1.52069 1.52073	1.54535 1.54538	1.56258 1.56257	1.62467 1.62458
5	1.52079 1.52061	1.54538 1.54521	----- -----	1.62456 -----
6	1.52039 1.52042	1.54522 1.54543	1.56240 1.56227	----- -----
7 ^c	1.52827 1.52904	----- -----	1.57011 1.56937	----- -----
7' ^c	1.51674 1.51770	----- -----	1.55937 1.55825	----- -----

a - The same relative differences persist at other temperatures.

b - The numbers refer to methods of preparation of PbO₂.

7 - Refers to Baker's 96.4% "analyzed" Lead Peroxide.

7' - Refers to Coleman and Bell's Lead Peroxide (Mn free).

c - Neither of these gave consistent results when subjected to treatment of No. (5)

Table II

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 0° and Constants of Equation (1), $E = E_0 + at + bt^2$.

Series A.			
$m(\text{H}_2\text{SO}_4)$	E_0	$-a \times 10^{-6}$	$b \times 10^{-8}$
0.0004985	1.42212	622.22	85.56
.0006979	1.43349	643.25	77.96
.0009971	1.44481	629.78	99.94
.001994	1.46704	604.20	93.39
.002992	1.47976	584.99	80.26
.004987	1.49514	575.59	76.82
.007147	1.50571	569.14	80.70
.010183	1.51591	548.94	67.54
.01998	1.53425	542.96	91.92
.03030	1.54491	510.33	74.28
.05009	1.55731	485.04	79.28
.07023	1.56564	471.79	78.73
.10068	1.57421	466.87	91.08
Series C.			
0.0005023	1.42214	667.35	94.33
.0007014	1.43302	669.46	118.98
.0010227	1.44546	623.58	81.28
.001988	1.46715	602.14	82.26
.002983	1.47974	583.39	81.46
.004982	1.49522	568.18	61.57
.006984	1.50495	567.42	76.51
.009969	1.51528	557.46	78.89
.02117	1.53578	532.29	85.12
.02996	1.54464	510.94	75.68
.04875	1.55665	496.81	99.15
.06834	1.56497	472.39	78.18
.09798	1.57365	459.29	75.37

Table II (continued)

Series B.

$m(\text{H}_2\text{SO}_4)$	E_o	$-a \times 10^{-6}$	$b \times 10^{-8}$
0.0004991	1.42235	669.21	102.54
.0006983	1.43327	652.48	87.82
.0009988	1.44468	632.04	92.08
.001967	1.46656	591.33	71.75
.002964	1.47929	583.04	74.73
.004891	1.49467	575.07	77.75
.006970	1.50491	561.15	58.00
.010068	1.51558	551.69	70.95
.01945	1.53356	539.76	81.56
.02948	1.54421	512.42	77.29
.04945	1.55700	487.53	83.51
.06943	1.56534	487.14	101.92
.10150	1.57440	466.24	100.01
.2001	1.59070	423.55	88.20
.5006(a)	1.61277	356.82	92.19
.9967	1.63197	304.83	75.30
1.5001	1.64564	266.62	63.12
2.006	1.65749	256.40	77.97
2.205	1.66200	258.90	89.07
3.044	1.68026	244.82	73.44
4.023	1.70046	249.88	78.91
4.980	1.71947	242.55	64.02
5.993	1.73844	242.04	53.91
7.093	1.75764	265.65	77.66

(a) The last figure of the electromotive force and of those that follow 0.5006 M are subscript.

Table III

(will be found on page 6.)

Table IV.

The Electromotive Forces of the Cell $\text{H}_2 | \text{H}_2\text{SO}_4(m) | \text{PbSO}_4 | \text{PbO}_2 | \text{Pt}$ at Round Concentrations at 0° and Constants of Equation

(2), $E = E_0 + ct + dt^2$.

$m(\text{H}_2\text{SO}_4)$	E_0	$-a \times 10^{-6}$	$b \times 10^{-8}$
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	1.49529	581.72	89.94
.007	1.50503	574.54	91.11
.01	1.51541	566.82	92.06
.02	1.53429	536.35	91.27
.03	1.54467	514.16	90.63
.05	1.55738	488.53	90.50
.07	1.56555	477.66	89.22
.10	1.57407	465.59	88.40
.20	1.59055	423.31	86.60
.50	1.61275	355.57	86.81
1.00	1.63214	303.83	76.43
1.50	1.64681	270.21	73.57
2.00	1.65728	251.86	75.30
3.00	1.67936	240.97	70.10
4.00	1.70009	240.48	66.20
5.00	1.72003	245.47	62.65
6.00	1.73861	248.59	62.96
7.00	1.75608	253.32	58.60

Table V

Calculated and Observed Values of E_0 .

$t, ^\circ\text{C.}$	$E_0(\text{Eq. 4})$ (obs. v.)	$E_0(\text{Eqs. 8-9})$ (obs. v.)	$E_0(\text{Eq. 5})$ (calc. v.)	$E_0(\text{Eq. 10})$ (calc. v.)	$-\Delta^*\text{mv.}$
0	1.6769 ₄	1.6769 ₄	1.67694	1.67694	0
5	1.6787 ₀	1.6784 ₆	1.67867	1.67842	0.25
10	1.6804 ₅	1.6799 ₈	1.68044	1.67997	0.47
15	1.6822 ₈	1.6815 ₉	1.68226	1.68156	0.70
20	1.6841 ₁	1.6832 ₂	1.68411	1.68322	0.89
25(a)	1.6859 ₇	1.6848 ₈	1.68601	1.68492	1.09
30	1.6880 ₀	1.6867 ₁	1.68796	1.68668	1.28
35	1.6899 ₂	1.6884 ₇	1.68994	1.68849	1.45
40	1.6919 ₆	1.6903 ₆	1.69196	1.69036	1.60
45	1.6939 ₆	1.6922 ₁	1.69402	1.69228	1.74
50	1.6961 ₆	1.6942 ₈	1.69613	1.69425	1.88
55	1.6983 ₁	1.6963 ₂	1.69827	1.69628	1.99
60	1.7004 ₄	1.6983 ₆	1.70046	1.69837	2.09

* Differences in mv. between fourth and fifth columns.

a - Gerke gives 1.7 v., and Vosburgh and Craig 1.681 v.

Table VI
Concentrations of the H^+ , HSO_4^- , and SO_4^{2-} ions and the
Ionic Strength of Sulfuric Acid Solutions

from 0 to 60°					
M(H_2SO_4)	$m_H \times 10^3$	<u>Zero Degrees</u>		μ	γ
		$m_{HSO_4} \times 10^3$	$m_{SO_4} \times 10^3$		
0.0005	0.9735	0.0265	0.4735	0.001447	0.843
.0007	1.3510	.0490	.6510	.002002	.818
.001	1.9075	.0925	.9075	.002815	.788
.002	3.7050	.2950	1.7050	.005410	.719
.003	5.408	.593	2.408	.007817	.673
.005	8.687	1.314	3.687	.012375	.607
.007	11.83	2.166	4.835	.016669	.560
.01	16.40	3.602	6.398	.022796	.508
.02	30.90	9.101	10.90	.041798	.400
.03	44.92	15.085	14.92	.059830	.334
.05	72.44	27.56	22.44	.094873	.251
.07	99.88	40.12	29.88	.12975	.199
.10	141.56	58.44	41.56	.18312	.147
<u>Five Degrees</u>					
0.0005	0.9725	0.0275	0.4725	0.001445	0.842
.0007	1.3495	.0505	.6495	.001999	.817
.001	1.9050	.0950	.9050	.002810	.787
.002	3.6875	.3125	1.6875	.005375	.718
.003	5.3945	.6055	2.3945	.007789	.671
.005	8.6575	1.3425	3.6575	.012315	.606
.007	11.791	2.209	4.791	.016582	.559
.01	16.3325	3.6675	6.3325	.022665	.507
.02	30.76	9.24	10.76	.04153	.399
.03	44.699	15.301	14.699	.059398	.333
.05	72.115	27.885	22.115	.09423	.250
.07	99.449	40.551	29.449	.128898	.198
.10	140.99	59.01	40.99	.18198	.146
<u>Ten Degrees</u>					
0.0005	0.9720	0.0280	0.4720	0.001444	0.841
.0007	1.3485	.0515	.6485	.001997	.816
.001	1.9025	.0975	.9025	.002805	.786
.002	3.6805	.3195	1.6805	.005361	.717
.003	5.3820	.6180	2.382	.007764	.670
.005	8.6355	1.3645	3.6355	.012271	.604
.007	11.758	2.242	4.758	.016516	.557
.01	16.283	3.717	6.283	.022566	.505
.02	30.662	9.338	10.662	.041324	.397
.03	44.556	15.445	14.556	.059111	.331
.05	71.902	28.098	21.902	.093804	.248
.07	99.184	40.816	29.184	.128368	.196
.10	140.695	59.305	40.695	.18139	.144

Table VI continued.

<u>Fifteen Degrees</u>					
$M(H_2SO_4)$	$m_H \times 10^{+3}$	$m_{HSO_4} \times 10^{+3}$	$m_{SO_4} \times 10^{+3}$	μ	γ
0.0005	0.9725	0.0275	0.4725	0.001445	0.840
.0007	1.3470	.0530	.6470	.001994	.815
.001	1.9000	.1000	.9000	.002800	.785
.002	3.6720	.3280	1.6720	.005344	.715
.003	5.3650	.6350	2.3650	.007730	.668
.005	8.6145	1.3855	3.6145	.012229	.602
.007	11.7105	2.2895	4.7105	.016421	.556
.01	16.215	3.785	6.215	.022430	.503
.02	30.527	9.473	10.527	.041054	.395
.03	44.36	15.64	14.36	.05872	.329
.05	71.56	28.44	21.56	.09312	.247
.07	98.727	41.273	28.727	.127454	.195
.10	140.08	59.92	40.08	.180163	.143
<u>Twenty Degrees</u>					
0.0005	0.9695	0.0305	0.4695	0.001439	0.839
.0007	1.3440	.0560	.6440	.001987	.814
.001	1.8950	.1050	.8950	.002790	.783
.002	3.6585	.3415	1.6585	.005317	.714
.003	5.3425	.6575	2.3425	.007685	.667
.005	8.5585	1.4415	3.5585	.012117	.601
.007	11.6395	2.3605	4.6395	.016279	.555
.01	16.105	3.895	6.105	.02221	.502
.02	30.375	9.6925	10.3075	.040615	.394
.03	44.035	15.965	14.035	.05807	.328
.05	71.043	28.957	21.043	.092085	.246
.07	98.727	41.273	28.727	.127454	.195
.10	140.08	59.92	40.08	.180163	.143
<u>Twenty-five Degrees</u>					
0.0005	0.9650	0.0350	0.4650	0.001430	0.838
.0007	1.3400	.0600	.6400	.001980	.813
.001	1.8900	.1100	.8900	.002780	.782
.002	3.6400	.3600	1.6400	.005280	.713
.003	5.317	.683	2.317	.007634	.665
.005	8.508	1.493	3.508	.01202	.600
.007	11.560	2.439	4.561	.016122	.553
.01	16.000	4.005	5.995	.021991	.501
.02	30.08	9.925	10.08	.04015	.393
.03	43.70	16.305	13.70	.05739	.327
.05	70.50	29.503	20.50	.090994	.245
.07	97.29	42.708	27.29	.12459	.193
.10	138.12	61.876	38.12	.17625	.141

Table VI continued.

$M(H_2SO_4)$	$m_H \times 10^{+3}$	$m_{HSO_4} \times 10^{+3}$	$m_{SO_4} \times 10^{+3}$	μ	γ
<u>Thirty Degrees</u>					
0.0005	0.9650	0.0350	0.4650	0.001430	0.837
.0007	1.3395	.0605	.6395	.001979	.811
.001	1.8845	.1155	.8845	.002769	.781
.002	3.628	.372	1.6280	.005256	.711
.003	5.2885	.7115	2.2885	.007577	.664
.005	8.454	1.546	3.454	.011908	.598
.007	11.484	2.516	4.484	.015968	.552
.01	15.885	4.115	5.885	.02177	.500
.02	29.829	10.171	9.829	.039658	.392
.03	43.333	16.667	13.333	.056665	.326
.05	69.922	30.078	19.922	.089843	.244
.07	96.516	43.484	26.516	.123032	.192
.10	137.063	62.937	37.063	.174126	.140
<u>Thirty-five Degrees</u>					
0.0005	0.9600	0.0400	0.460	0.001420	0.836
.0007	1.3345	.0655	.655	.001969	.810
.001	1.8775	.1225	.8775	.002755	.779
.002	3.6075	.3925	1.6075	.005215	.710
.003	5.2525	.7475	2.2525	.007505	.663
.005	8.3855	1.6145	3.3855	.011771	.597
.007	11.382	2.618	4.382	.015764	.551
.01	15.723	4.277	5.723	.021446	.499
.02	29.526	10.474	9.526	.039052	.391
.03	42.889	17.111	12.889	.055778	.325
.05	69.215	30.785	19.215	.08843	.243
.07	95.563	44.437	25.563	.121126	.191
.10	135.50	64.50	35.50	.17100	.140
<u>Forty Degrees</u>					
0.0005	0.9615	0.0385	0.4615	0.001423	0.834
.0007	1.3300	.0700	.6300	.001960	.808
.001	1.8695	.1305	.8695	.002739	.778
.002	3.586	.4140	1.586	.005172	.708
.003	5.215	.7850	2.215	.007430	.661
.005	8.313	1.687	3.313	.011626	.596
.007	11.2775	2.7225	4.2775	.015553	.549
.01	15.57	4.430	5.570	.021140	.497
.02	29.213	10.787	9.2125	.038425	.390
.03	42.43	17.57	12.43	.05486	.324
.05	68.494	31.506	18.494	.086988	.242
.07	94.587	45.413	24.587	.119174	.190
.10	134.000	66.000	34.000	.16800	.139
<u>Forty-five Degrees</u>					
0.0005	0.9550	0.0450	0.4550	0.001410	0.833
.0007	1.3245	.0755	.6245	.001949	.807
.001	1.8600	.1400	.8600	.002720	.776
.002	3.5585	.4415	1.5585	.005117	.706
.003	5.168	.8320	2.168	.007336	.659
.005	8.225	1.7750	3.2250	.011450	.594

Table VI continued.

Forty-five Degrees.

$M(H_2SO_4)$	$m_H \times 10^{+3}$	$m_{HSO_4} \times 10^{+3}$	$m_{SO_4} \times 10^{+3}$	μ	γ
0.007	11.147	2.853	4.147	0.015294	0.548
.01	15.379	4.621	5.379	.020758	.496
.02	28.8365	11.1635	8.8365	.037673	.389
.03	41.869	18.131	11.869	.053737	.324
.05	67.593	32.407	17.593	.085185	.242
.07	93.353	46.647	23.353	.116706	.190
.10	132.526	67.474	32.526	.165052	.139

Fifty Degrees

0.0005	0.9545	0.0455	0.4545	0.0014090	0.832
.0007	1.3174	.0826	.6174	.0019348	.806
.001	1.8470	.1530	.8470	.002694	.775
.002	3.523	.4770	1.5230	.005046	.705
.003	5.1065	.8935	2.1065	.007213	.659
.005	8.1115	1.8885	3.1115	.011223	.594
.007	10.987	3.013	3.9865	.014973	.548
.01	15.135	4.865	5.135	.020270	.497
.02	28.350	11.640	8.360	.036719	.390
.03	41.172	18.828	11.172	.052344	.325
.05	66.477	33.523	16.477	.082954	.243
.07	91.815	48.185	21.815	.11363	.191
.10	130.45	69.547	30.453	.160905	.139

Fifty-five Degrees

0.0005	0.94925	0.05075	0.44925	0.0013985	0.830
.0007	1.3083	.09170	.60830	.0019166	.804
.001	1.83135	.16865	.83135	.0026627	.773
.002	3.48035	.51965	1.48035	.0049607	.704
.003	5.034	.9660	2.034	.007068	.658
.005	7.979	2.021	2.979	.010959	.594
.007	10.790	3.210	3.790	.01458	.548
.01	14.788	5.213	4.787	.019575	.498
.02	27.817	12.183	7.817	.035634	.391
.03	40.384	19.616	10.384	.050768	.325
.05	65.284	34.719	15.281	.080564	.243
.07	90.186	49.815	20.186	.110371	.191
.10	128.153	71.847	28.153	.156306	.139

Sixty Degrees

0.0005	0.9421	0.0579	0.4421	0.0013842	0.829
.0007	1.2959	.1041	.5959	.0018918	.803
.001	1.8098	.1902	.8098	.0026196	.773
.002	3.424	.576	1.424	.004848	.704
.003	4.941	1.059	1.941	.0068785	.658
.005	7.809	2.191	2.809	.010618	.595
.007	10.55	3.453	3.547	.014094	.550
.01	14.51	5.490	4.514	.019028	.499
.02	27.17	12.83	7.165	.034330	.393
.03	39.46	20.55	9.455	.04891	.328
.05	63.77	36.23	13.77	.077532	.246
.07	88.10	51.90	18.10	.10619	.194
.10	125.38	74.62	25.38	.15076	.142

Table VII
The Activity of Water in Sulfuric Acid from 0 to 60°.

M(H ₂ SO ₄)	0°	5°	10°	15°	20°	25°	30°
0.0005	0.99998	0.99998	0.99998	0.99998	0.99998	0.99998	0.99998
.0007	.99996	.99996	.99996	.99996	.99996	.99996	.99996
.001	.99995	.99995	.99995	.99995	.99995	.99995	.99995
.002	.99990	.99990	.99990	.99990	.99990	.99990	.99990
.003	.99987	.99987	.99987	.99987	.99987	.99987	.99987
.005	.99979	.99979	.99979	.99979	.99979	.99979	.99979
.007	.99970	.99970	.99970	.99970	.99970	.99971	.99971
.01	.99959	.99959	.99959	.99959	.99960	.99960	.99960
.02	.99922	.99922	.99923	.99924	.99925	.99926	.99926
.03	.99883	.99884	.99885	.99887	.99888	.99889	.99889
.05	.99809	.99811	.99813	.99815	.99817	.99819	.99820
.07	.99732	.99735	.99738	.99741	.99744	.99748	.99749
.10	.99620	.99624	.99628	.99632	.99635	.99638	.99639
.20	.99262	.99268	.99274	.99280	.99284	.99288	.99291
.50	.98168	.98177	.98188	.98193	.98200	.98206	.98211
1.00	.96132	.96145	.96159	.96173	.96186	.96200	.96214
1.50	.93743	.93778	.93812	.93846	.93880	.93914	.93948
2.00	.91046	.91096	.91172	.91235	.91298	.91362	.91424
3.00	.84376	.84512	.84648	.84785	.84921	.85060	.85200
4.00	.76502	.76749	.77000	.77251	.77500	.77750	.77999
5.00	.68008	.68361	.68723	.69079	.69440	.69796	.70149
6.00	.59681	.60140	.60612	.61079	.61532	.62003	.62439
7.00	.51814	.52342	.52889	.53438	.53977	.54529	.55049

M(H ₂ SO ₄)	35°	40°	45°	50°	55°	60°
0.0005	0.99998	0.99998	0.99998	0.99998	0.99998	0.99998
.0007	.99996	.99996	.99996	.99996	.99996	.99996
.001	.99995	.99995	.99995	.99995	.99995	.99995
.002	.99990	.99990	.99990	.99990	.99990	.99990
.003	.99987	.99987	.99987	.99988	.99988	.99988
.005	.99979	.99979	.99979	.99980	.99980	.99980
.007	.99971	.99971	.99972	.99972	.99972	.99972
.01	.99961	.99961	.99961	.99962	.99962	.99962
.02	.99927	.99927	.99928	.99928	.99929	.99929
.03	.99890	.99891	.99892	.99892	.99893	.99893
.05	.99820	.99821	.99822	.99822	.99823	.99823
.07	.99750	.99750	.99751	.99751	.99752	.99752
.10	.99640	.99640	.99641	.99641	.99642	.99642
.20	.99293	.99294	.99295	.99296	.99297	.99298
.50	.98215	.98219	.98223	.98227	.98230	.98234
1.00	.96228	.96241	.96254	.96268	.96282	.96296
1.50	.93982	.94016	.94050	.94084	.94118	.94152
2.00	.91487	.91548	.91612	.91674	.91736	.91798
3.00	.85339	.85478	.85615	.85751	.85884	.86022
4.00	.78243	.78499	.78743	.79000	.79242	.79497
5.00	.70508	.70860	.71220	.71574	.71931	.72293
6.00	.62879	.63311	.63743	.64179	.64619	.65051
7.00	.55565	.56077	.56594	.57110	.57632	.58150

Table VIII

The Stoichiometrical Activity Coefficients of Aqueous

Sulfuric Acid Solutions from 0 to 60°
Calculated by Equation (3).

M(H ₂ SO ₄)	0°	5°	10°	15°	20°	25°	30°
0.0005	0.908	0.898	0.886	0.876	0.866	0.857	0.849
.0007	.892	.879	.867	.855	.844	.833	.824
.001	.873	.858	.843	.830	.816	.804	.793
.002	.825	.805	.786	.768	.752	.736	.722
.003	.788	.766	.745	.725	.706	.689	.673
.005	.734	.708	.684	.662	.641	.621	.603
.007	.691	.664	.639	.616	.594	.574	.556
.01	.649	.621	.595	.572	.549	.529	.510
.02	.554	.527	.503	.480	.459	.440	.422
.03	.495	.470	.448	.427	.407	.390	.373
.05	.426	.403	.383	.364	.346	.330	.316
.07	.383	.361	.342	.324	.308	.293	.280
.10	.341	.321	.303	.287	.272	.258	.245
.20	.271	.255	.240	.227	.214	.203	.193
.50	.202	.189	.178	.168	.158	.150	.142
1.00	.173	.161	.151	.142	.134	.126	.119
1.50	.167	.155	.145	.136	.128	.121	.114
2.00	.170	.158	.147	.138	.129	.121	.114
3.00	.201	.185	.171	.159	.147	.137	.128
4.00	.254	.232	.212	.195	.180	.166	.154
5.00	.330	.299	.271	.247	.226	.207	.190
6.00	.427	.383	.345	.312	.283	.257	.234
7.00	.546	.486	.435	.390	.351	.317	.287
M(H ₂ SO ₄)	35°	40°	45°	50°	55°	60°	
0.0005	0.840	0.833	0.824	0.818	0.812	0.805	
.0007	.814	.805	.796	.789	.781	.773	
.001	.782	.772	.762	.753	.745	.736	
.002	.707	.694	.681	.670	.659	.648	
.003	.658	.643	.629	.617	.605	.593	
.005	.586	.570	.555	.541	.521	.508	
.007	.538	.522	.506	.492	.479	.466	
.01	.492	.476	.460	.446	.433	.420	
.02	.406	.391	.376	.363	.351	.339	
.03	.358	.344	.331	.319	.308	.297	
.05	.302	.290	.278	.267	.257	.248	
.07	.267	.255	.245	.235	.226	.217	
.10	.234	.223	.213	.204	.196	.188	
.20	.183	.174	.166	.159	.152	.146	
.50	.135	.128	.122	.116	.111	.106	
1.00	.113	.107	.102	.0962	.0921	.0878	
1.50	.107	.102	.0963	.0914	.0870	.0828	
2.00	.107	.101	.0958	.0908	.0862	.0818	
3.00	.120	.112	.105	.0991	.0935	.0882	
4.00	.143	.133	.124	.115	.108	.101	
5.00	.175	.161	.149	.138	.129	.120	
6.00	.214	.197	.181	.167	.154	.143	
7.00	.261	.238	.217	.199	.183	.168	

Table IX
 The Stoichiometrical Activity Coefficients of Aqueous
 Sulfuric Acid Solutions from 0 to 60°
 Calculated by Equation (3) and
 Second E_0 Values.

$M(H_2SO_4)$	0°	5°	10°	15°	20°	25°	30°	35°
0.0005	0.912	0.908	0.901	0.896	0.890	0.885	0.880	0.874
.0007	.896	.889	.880	.875	.867	.857	.854	.848
.001	.876	.867	.857	.848	.839	.830	.823	.814
.002	.825	.811	.796	.783	.769	.757	.746	.733
.003	.788	.771	.754	.739	.723	.709	.695	.682
.005	.734	.713	.693	.674	.656	.639	.623	.608
.007	.691	.669	.647	.627	.608	.591	.574	.558
.01	.649	.626	.603	.582	.562	.544	.527	.510
.02	.554	.531	.509	.489	.470	.453	.437	.421
.03	.495	.474	.453	.435	.417	.401	.386	.371
.05	.426	.406	.387	.371	.354	.340	.326	.313
.07	.383	.364	.346	.330	.315	.301	.290	.277
.10	.341	.324	.307	.293	.278	.265	.254	.243
.20	.271	.257	.243	.231	.219	.209	.199	.190
.50	.202	.191	.181	.171	.162	.154	.147	.140
1.00	.173	.163	.153	.145	.137	.130	.123	.117
1.50	.167	.157	.147	.139	.131	.124	.117	.111
2.00	.170	.159	.149	.140	.132	.124	.118	.111
3.00	.201	.186	.173	.162	.151	.141	.132	.124
4.00	.254	.233	.215	.199	.184	.171	.159	.148
5.00	.330	.301	.275	.252	.231	.212	.196	.181
6.00	.427	.386	.350	.318	.289	.264	.242	.222
7.00	.546	.490	.440	.397	.359	.326	.297	.271
$M(H_2SO_4)$	40°	45°	50°	55°	60°			
0.0005	0.869	0.863	0.859	0.854	0.848			
.0007	.841	.834	.828	.822	.814			
.001	.806	.797	.790	.783	.775			
.002	.722	.711	.701	.691	.680			
.003	.669	.656	.645	.634	.622			
.005	.593	.579	.566	.547	.533			
.007	.543	.528	.515	.502	.489			
.01	.495	.480	.467	.454	.441			
.02	.407	.393	.380	.368	.356			
.03	.358	.345	.333	.322	.311			
.05	.301	.290	.279	.270	.260			
.07	.266	.256	.246	.238	.228			
.10	.227	.223	.214	.205	.197			
.20	.181	.173	.166	.159	.153			
.50	.133	.127	.122	.117	.107			
1.00	.111	.106	.101	.0966	.0922			
1.50	.106	.101	.0956	.0911	.0869			
2.00	.105	.100	.0949	.0903	.0859			
3.00	.117	.110	.104	.0980	.0926			
4.00	.138	.129	.121	.113	.106			
5.00	.168	.156	.145	.135	.126			
6.00	.205	.189	.174	.161	.150			
7.00	.247	.227	.208	.192	.177			

Fig. 1.

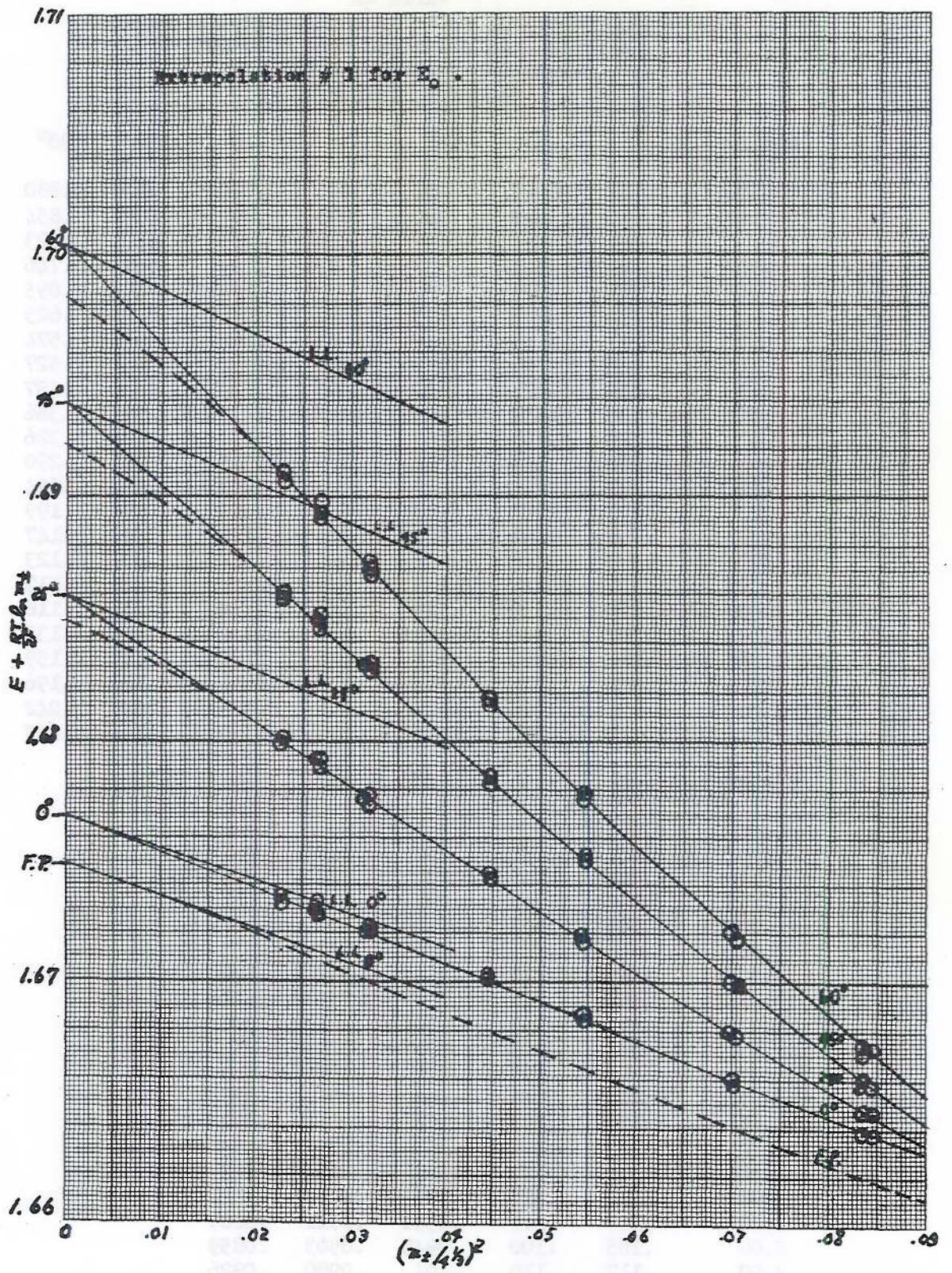


Fig. 2.

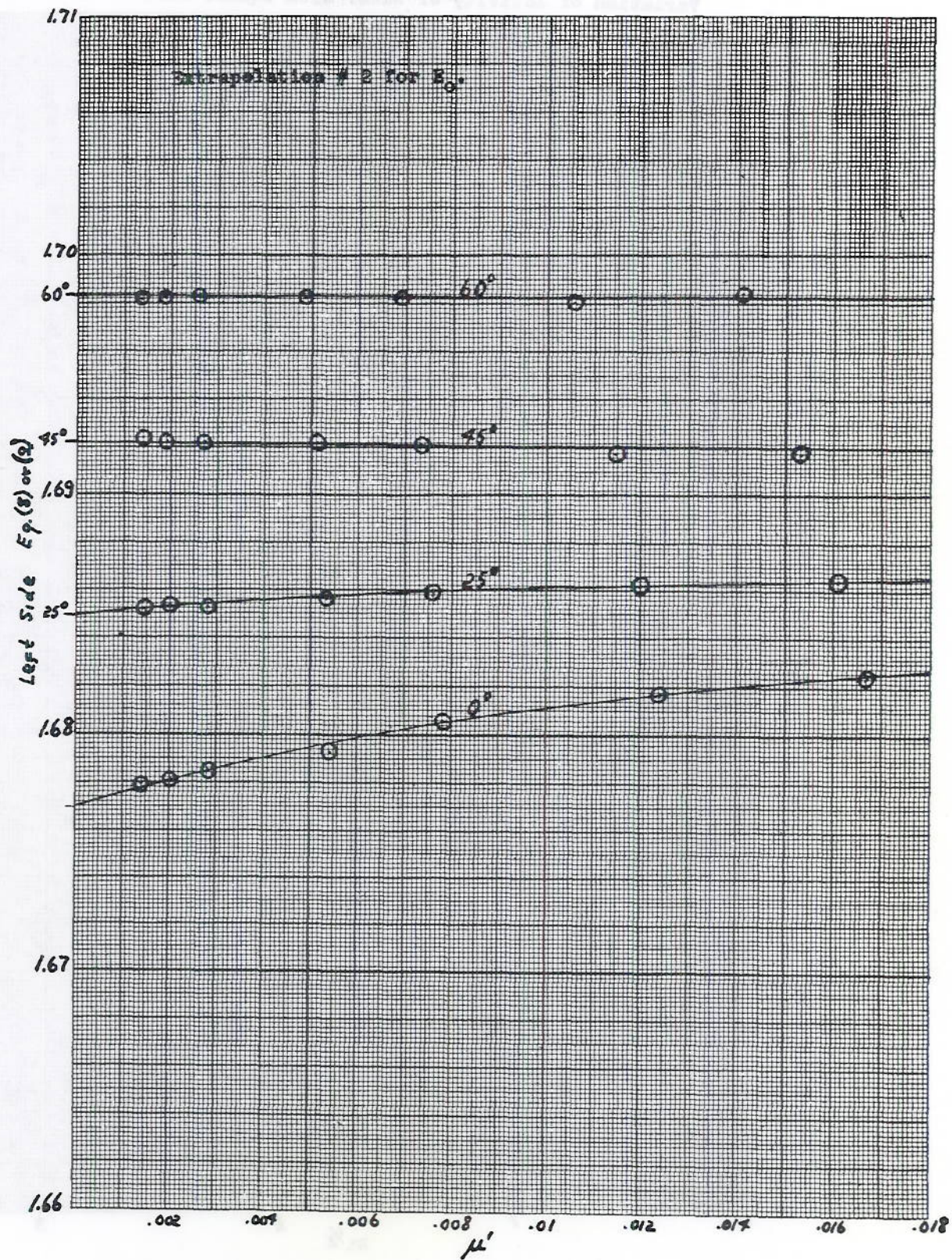
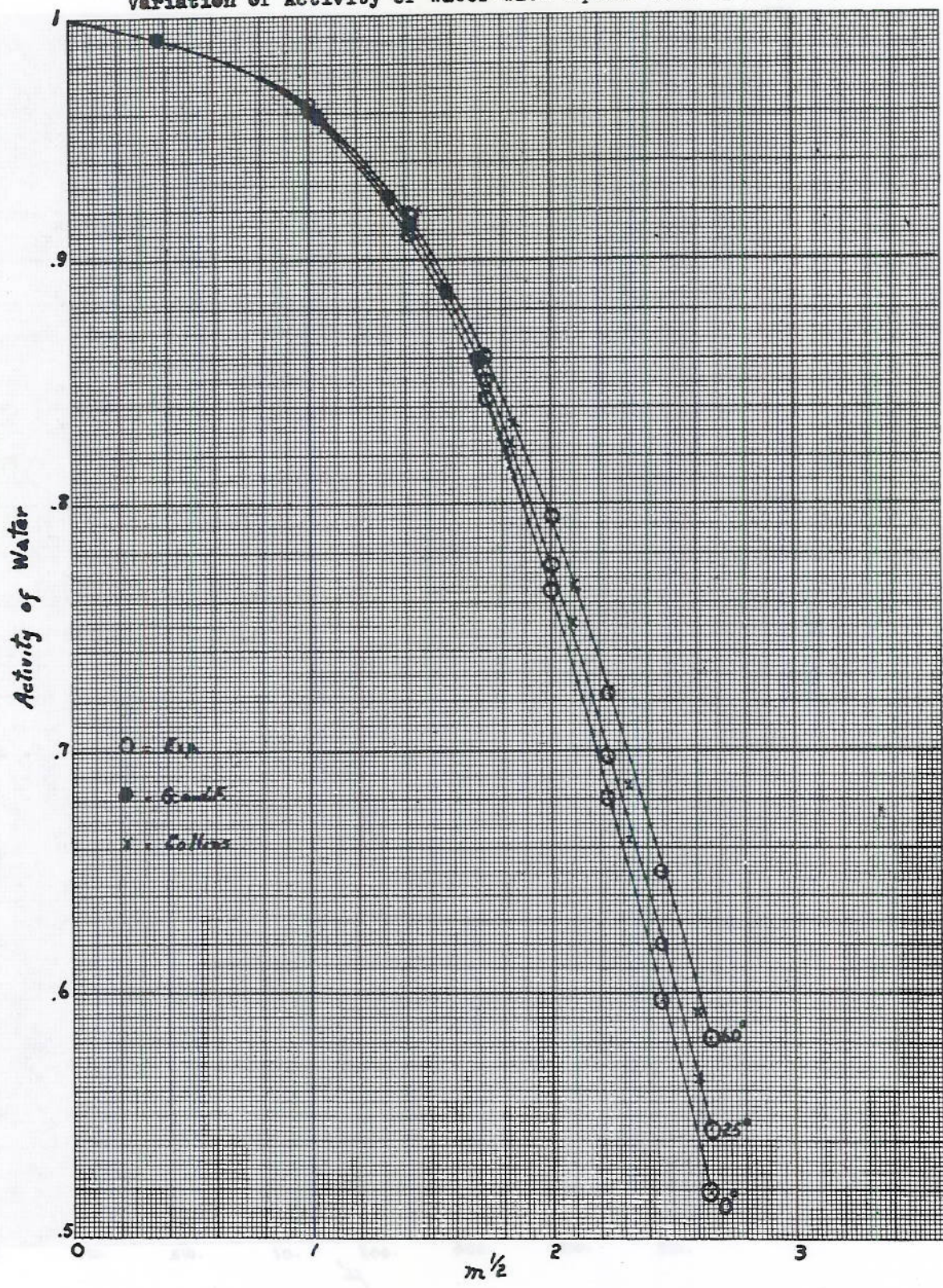
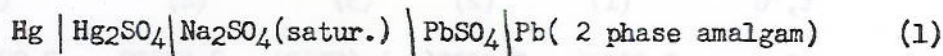


Fig. 3.
Variation of Activity of Water with square root of Molality.



A Thermodynamic Study of the Lead Accumulator from 0 to 60°.

In order to evaluate the potentials of the positive and negative electrodes of the lead accumulator, measurements were made of the galvanic cell



These electromotive forces are given in Table I. Since the mercury-mercurous sulfate electrode potential has been obtained in a preceding paper, we can obtain the potential of the other electrode of above cell by difference. The difference between the amalgamated lead electrode and a pure spongy electrode may be obtained from the measurements of Gerke.

Gerke, J. Am. Chem. Soc., 44, 1684 (1922)

In Table II, we have given the electrode potentials of the two electrodes and the normal electrode potential of the accumulator. We have also given the difference in voltage produced by amalgamating the negative electrode. The negative electrode potential was not obtained by comparing a Pb/PbSO₄ electrode against hydrogen, as this electrode was found to polarize in sulfuric acid solutions. This polarization varied with concentration and became as high as 0.002 v in dilute solutions.

In Tables III and IV we have given the voltage of the accumulator at various molalities and specific gravities. These values, of course, are for an "ideal lead accumulator" constructed of chemically pure materials. Entropy of reaction and of lead have not been incorporated.

Table I
The Electromotive Forces of the Cell $\text{Hg} \mid \text{Hg}_2\text{SO}_4 \mid \text{Na}_2\text{SO}_4(\text{sat.}) \mid \text{PbSO}_4 \mid \text{Pb}(\text{ 2 phase amalgam})$ and Least Squared Values.^a

t, °C.	E	E(Least square)	Δ mv.
0	0.96051	0.96051	0
5	.96129	.96129	0
10	.96208	.96210	+0.02
15	.96293	.96292	-0.01
20	.96375	.96376	+0.01
25	.96462	.96462	0
30	.96549	.96550	+0.01
35	.96639	.96640	+0.01
40	.96731	.96733	+0.02
45	.96825	.96825	0
50	.96921	.96921	0
55	.97019	.97018	-0.01
60	.97119	.97118	-0.01

$$E = 0.96462 + 0.00017(t-25) + 0.0000004(t-25)^2 = \text{least square equation.}$$

a - Measurements with NiSO₄ gave same results as Na₂SO₄.

Table II

Electrode Potentials of + and - Plates of Lead Accumulator
and Normal Electrode Potential.

t, °C	(1)	(2)	(3)	(4)	(5)	Δ *v.
0	0.32556	0.33096	1.679694	2.00250	2.00790	0.00540
5	.33053	.33601	1.67867	2.00920	2.01468	.00548
10	.33553	.34109	1.68044	2.01597	2.02153	.00556
15	.34054	.34618	1.68226	2.02280	2.02844	.00564
20	.34555	.35127	1.68411	2.02966	2.03538	.00572
25	.35060	.35640	1.68601	2.03661	2.04241	.00580
30	.35567	.36155	1.68796	2.04363	2.04951	.00588
35	.36075	.36671	1.68994	2.05069	2.05665	.00596
40	.36587	.37191	1.69196	2.05783	2.06387	.00604
45	.37097	.37709	1.69402	2.06499	2.07111	.00612
50	.37610	.38230	1.69613	2.07223	2.07843	.00620
55	.38126	.38754	1.69827	2.07953	2.08581	.00628
60	.38644	.39280	1.70046	2.08690	2.09326	.00636

(1) - Amalgamated negative electrode, (Pb-Hg, PbSO₄)

(2) - Negative electrode, (Pb, PbSO₄)

(3) - Positive electrode, (PbO₂, PbSO₄)

(4) - Normal electrode potentials of amalgamated battery.

(5) - Normal electrode potential of battery.

* - Difference in voltage between amalgamated and non-amalgamated lead accumulator.

Table III

Variation of Voltage of Lead Accumulator with Molality in Measured Range from 0 to 60°.

m(H ₂ SO ₄)	0°	5°	10°	15°	20°	25°	30°
0.05	1.76873	1.76721	1.76576	1.76438	1.76306	1.76182	1.76062
.10	1.80207	1.80077	1.79955	1.79839	1.79724	1.79626	1.79529
.20	1.83495	1.83408	1.83328	1.83253	1.83184	1.83122	1.83068
.50	1.87908	1.87888	1.87876	1.87867	1.87867	1.87874	1.87885
1.00	1.91737	1.91766	1.91804	1.91845	1.91892	1.91945	1.92004
1.50	1.94412	1.94475	1.94544	1.94620	1.94697	1.94780	1.94869
2.00	1.96637	1.96720	1.96808	1.96901	1.96998	1.97100	1.97210
3.00	2.00874	2.00964	2.01072	2.01162	2.01278	2.01379	2.01494
4.00	2.04790	2.04881	2.04987	2.05077	2.05182	2.05291	2.05403
5.00	2.08501	2.08587	2.08678	2.08772	2.08870	2.08973	2.09080
6.00	2.11909	2.11992	2.12081	2.12162	2.12270	2.12368	2.12474
7.00	2.15071	2.15150	2.15234	2.15234	2.15410	2.15502	2.15601

m(H ₂ SO ₄)	35°	40°	45°	50°	55°	60°
0.05	1.75952	1.75848	1.75748	1.75656	1.75570	1.75495
.10	1.79440	1.79358	1.79279	1.79208	1.79144	1.79086
.20	1.83019	1.82978	1.82939	1.82911	1.82887	1.82870
.50	1.87904	1.87931	1.87959	1.87997	1.88040	1.88091
1.00	1.92066	1.92138	1.92211	1.92270	1.92375	1.92467
1.50	1.94963	1.95065	1.95167	1.95277	1.95390	1.95511
2.00	1.97312	1.97442	1.97563	1.97693	1.97825	1.97964
3.00	2.01614	2.01741	2.01868	2.02004	2.02142	2.02288
4.00	2.05513	2.05647	2.05773	2.05905	2.06042	2.06184
5.00	2.09190	2.09309	2.09428	2.09552	2.09681	2.09814
6.00	2.12582	2.12696	2.12814	2.12936	2.13061	2.13192
7.00	2.15704	2.15810	2.15920	2.16035	2.16153	2.16276

Variation of Voltage of Lead Accumulator with Specific Gravity in Limited Range at 25° Centigrade.

Sp.Gr.	1.02	1.03	1.04	1.05	1.10	1.15	1.25
E.M.F.	1.854	1.878	1.894	1.907	1.961	2.005	2.098
Dolezalek.	-	-	-	1.906	1.965	2.010	2.094
Kendrick.	1.845	1.871	1.890	1.905	1.957	2.000	2.085
Vinal and Altrup.	-	-	1.890	1.903	1.956	2.000	2.091
Gladstone and Hibbert.	1.788	1.851	1.890	1.913	1.963	2.003	2.069

The Thermodynamics of Aqueous Sulfuric Acid Solutions
from Electromotive Force Measurements.

by

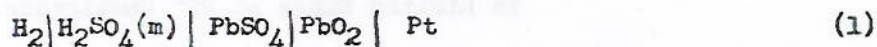
Herbert S. Harned and Walter J. Hamer

In recent years, the electromotive force method has been extensively employed to determine the relative partial heat contents and heat capacities of acids, bases, salts and acid-salt mixtures in aqueous solutions

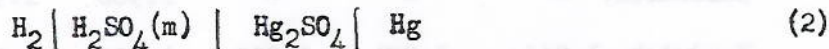
Harned and Ehlers, J. Am. Chem. Soc., 55, 2179 (1933)
Harned and Nims, *ibid.*, 54, 423 (1932)
Harned and Hecker, *ibid.*; 55, 4838 (1933); 56, 650 (1934)
Harned and Hamer, *ibid.*, 55, 2194 (1933); 55, 4496 (1933)
Cowperthwaite, LaMer and Barksdale, *ibid.*, 56, 544 (1934)
LaMer and Parks, *ibid.*, 53, 2040 (1931); 55, 4343 (1933)
LaMer and Cowperthwaite, *ibid.*, 54, 4114 (1932); 54, 4754 (1932)
Pearce and Hart, *ibid.*, 43, 2483 (1921)
Ellis, *ibid.*, 38, 737 (1916)
Noyes and Ellis, *ibid.*, 39, 2532 (1917) and others.

Fair check and in some cases excellent agreement has been obtained with calorimetric data.

It is the purpose of this contribution to investigate the applicability of the electromotive force method to the determination of these heat data for a partially dissociated unsymmetric valence type electrolyte, namely the dibasic acid, sulfuric. These data are also important for industrial purposes, and measurements have consequently been extended over a wide concentration and temperature range. In the preceding paper measurements of the galvanic cell



were given for the concentration range of 0.0005 to 7.0 M and throughout the temperature range of from 0 to 60°. These data will be supplemented by measurements of the galvanic cell



which was measured over the same temperature range and extended to higher concentrations. This cell was measured from 0.003 to 17.5 M.

Experimental Procedure.

Mercury: - Mercury washed twice in dilute nitric acid and twice distilled in vacuo was employed.

Table III

Variation of Voltage of Lead Accumulator with Molality in Measured Range from 0 to 60°.

m(H ₂ SO ₄)	0°	5°	10°	15°	20°	25°	30°
0.05	1.76873	1.76721	1.76576	1.76438	1.76306	1.76182	1.76062
.10	1.80207	1.80077	1.79955	1.79839	1.79724	1.79626	1.79529
.20	1.83495	1.83408	1.83328	1.83253	1.83184	1.83122	1.83068
.50	1.87908	1.87888	1.87876	1.87867	1.87867	1.87874	1.87885
1.00	1.91737	1.91766	1.91804	1.91845	1.91892	1.91945	1.92004
1.50	1.94412	1.94475	1.94544	1.94620	1.94697	1.94780	1.94869
2.00	1.96637	1.96720	1.96808	1.96901	1.96998	1.97100	1.97210
3.00	2.00874	2.00964	2.01072	2.01162	2.01278	2.01379	2.01494
4.00	2.04790	2.04881	2.04987	2.05077	2.05182	2.05291	2.05403
5.00	2.08501	2.08587	2.08678	2.08772	2.08870	2.08973	2.09080
6.00	2.11909	2.11992	2.12081	2.12162	2.12270	2.12368	2.12474
7.00	2.15071	2.15150	2.15234	2.15234	2.15410	2.15502	2.15601

m(H ₂ SO ₄)	35°	40°	45°	50°	55°	60°
0.05	1.75952	1.75848	1.75748	1.75656	1.75570	1.75495
.10	1.79440	1.79358	1.79279	1.79208	1.79144	1.79086
.20	1.83019	1.82978	1.82939	1.82911	1.82887	1.82870
.50	1.87904	1.87931	1.87959	1.87997	1.88040	1.88091
1.00	1.92066	1.92138	1.92211	1.92270	1.92375	1.92467
1.50	1.94963	1.95065	1.95167	1.95277	1.95390	1.95511
2.00	1.97312	1.97442	1.97563	1.97693	1.97825	1.97964
3.00	2.01614	2.01741	2.01868	2.02004	2.02142	2.02288
4.00	2.05513	2.05647	2.05773	2.05905	2.06042	2.06184
5.00	2.09190	2.09309	2.09428	2.09552	2.09681	2.09814
6.00	2.12582	2.12696	2.12814	2.12936	2.13061	2.13192
7.00	2.15704	2.15810	2.15920	2.16035	2.16153	2.16276

Variation of Voltage of Lead Accumulator with Specific Gravity in Limited Range at 25° Centigrade.

Sp.Gr.	1.02	1.03	1.04	1.05	1.10	1.15	1.25
E.M.F.	1.854	1.878	1.894	1.907	1.961	2.005	2.098
Dolezalek.	-	-	-	1.906	1.965	2.010	2.094
Kendrick.	1.845	1.871	1.890	1.905	1.957	2.000	2.085
Vinal and Altrup.	-	-	1.890	1.903	1.956	2.000	2.091
Gladstone and Hibbert.	1.788	1.851	1.890	1.913	1.963	2.003	2.069

The Thermodynamics of Aqueous Sulfuric Acid Solutions
from Electromotive Force Measurements.

by

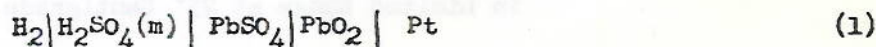
Herbert S. Harned and Walter J. Hamer

In recent years, the electromotive force method has been extensively employed to determine the relative partial heat contents and heat capacities of acids, bases, salts and acid-salt mixtures in aqueous solutions

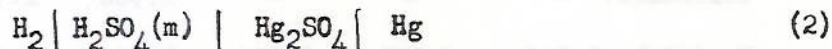
Harned and Ehlers, J. Am. Chem. Soc., 55, 2179 (1933)
Harned and Nims, *ibid.*, 54, 423 (1932)
Harned and Hecker, *ibid.*, 55, 4838 (1933); 56, 650 (1934)
Harned and Hamer, *ibid.*, 55, 2194 (1933); 55, 4496 (1933)
Cowperthwaite, LaMer and Barksdale, *ibid.*, 56, 544 (1934)
LaMer and Parks, *ibid.*, 53, 2040 (1931); 55, 4343 (1933)
LaMer and Cowperthwaite, *ibid.*, 54, 4114 (1932); 54, 4754 (1932)
Pearce and Hart, *ibid.*, 43, 2483 (1921)
Ellis, *ibid.*, 38, 737 (1916)
Noyes and Ellis, *ibid.*, 39, 2532 (1917) and others.

Fair check and in some cases excellent agreement has been obtained with calorimetric data.

It is the purpose of this contribution to investigate the applicability of the electromotive force method to the determination of these heat data for a partially dissociated unsymmetric valence type electrolyte, namely the dibasic acid, sulfuric. These data are also important for industrial purposes, and measurements have consequently been extended over a wide concentration and temperature range. In the preceding paper measurements of the galvanic cell



were given for the concentration range of 0.0005 to 7.0 M and throughout the temperature range of from 0 to 60°. These data will be supplemented by measurements of the galvanic cell



which was measured over the same temperature range and extended to higher concentrations. This cell was measured from 0.003 to 17.5 M.

Experimental Procedure.

Mercury: - Mercury washed twice in dilute nitric acid and twice distilled in vacuo was employed.

Mercurous Sulfate: - Mercurous sulfate was prepared by the flowing anode method described by Hulett.

Hulett, Phy. Rev., 32, 257 (1911)

This method of preparation was employed as it gives a fine grain size of mercurous sulfate which shows little or no hysteresis

Vosburgh and Eppley, J. Am. Chem. Soc., 46, 104 (1924); 45, 2268 (1923)

and hydrolyzes to a lesser degree

Summers and Gardiner, Trans. Am. Electrochem. Soc., 56, 18 (1929)
Gardiner and Hulett, *ibid*, 46, 17 (1919)

The mercurous sulfate was digested under 3 M sulfuric acid as suggested by Vosburgh and Eppley

Vosburgh and Eppley, J. Am. Chem. Soc., 46, 104 (1924), page 110

The final preparation was kept under 0.02 M sulfuric acid and in the absence of light until employed in the cell.

Cells and Bubble Tubes: - The apparatus described in preceding paper was employed for these measurements.

Sulfuric Acid, Hydrogen, and Hydrogen Electrodes: - These are described in preceding paper. Concentrated solutions of sulfuric acid are not reduced by hydrogen. Randall and Cushman

Randall and Cushman, J. Am. Chem. Soc., 40, 393 (1918)

also found no reduction.

Mercury-Mercurous Sulfate Electrodes: - The mercury-mercurous sulfate electrodes were prepared in a manner similar to the construction of the lead dioxide-lead sulfate electrodes described by the authors in the preceding paper. In this case the redistilled mercury was placed over the sealed in platinum wire and the mercurous sulfate paste well washed with cell solution was placed over the mercury and the acid was introduced carefully to avoid wetting of the platinum wire.

Behavior of Cells: - The cells were constant and were reproducible to within ± 0.05 mv. on the average although some individual cells were found to deviate ± 0.1 mv. among themselves. The electrodes are not affected by air and may be used for acid concentrations above 0.002 M. Below this concentration hydrolysis occurs and basic mercurous sulfate is in equilibrium with the normal salt. Hysteresis was not observed and to be more certain of its elimination measurements were made after an increase in temperature and not after a decrease. Measurements were made in course of a day. After two days a yellow basic sulfate appears due to effect of light. Cells were also kept as stable as possible to decrease possibility of mercuric ion formation

Wolff and Waters, Bur. Standards Bull., 4, 81 (1907)

In this case new electrodes were employed for all measurements, and even though vacuum technique is not necessary, the cells were filled in vacuo.

The Electromotive Forces of the Cells $\text{H}_2|\text{H}_2\text{SO}_4(m)|\text{Hg}_2\text{SO}_4|\text{Hg}$ above 0.05 M:-

Since a comprehensive series of measurements were made and for the sake of brevity we have smoothed these results by the method described in the preceding paper. These may be expressed as a function of temperature by the equation

$$E = E_{25} + a(t - 25) + b(t - 25)^2 \quad (3)$$

where E is the electromotive force at a temperature t° and a and b are constants. These constants were obtained by the method of least squares. The values of E_{25} corrected to one atmosphere hydrogen pressure employing the vapor pressures referred to in preceding paper and the values of a and b are given in Table I. The electromotive forces are given at 25° so that a direct comparison may be made with measurements of previous experimenters.

Brønsted, Z. physik. Chem., 68, 693 (1910)
Lewis and Lacey, J. Am. Chem. Soc., 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)

Measurements below 0.05 M are not given in Table I. Although the potentials are constant and reproducible to ± 0.1 mv., the solubility of mercurous sulfate amounts to 100% at 0.003 M and the method in which corrections should be made is obscure. The total sulfate-ion concentration may be calculated as described in preceding paper but the effect of the mercurous ion cannot be neglected, an effect not definitely known. In fact we have a liquid junction and the data gives the activity coefficient of sulfuric acid in sulfuric acid-mercurous sulfate mixtures and distort the normal extrapolation to be expected for pure acid solutions.

Evaluation of the Normal Electrode Potential, E_0 , of the Mercury-Mercurous Sulfate Electrode: - Since no reliance may be placed in the dilute solution measurements we have obtained the E_0 of the mercury-mercurous sulfate electrode by equation (12) of the preceding paper after the electromotive forces of the cell $H_2|H_2SO_4(m) | PbSO_4| PbO_2| Pt$ were corrected for the activity of water. E_0 was calculated for 0.05, 0.07 and 0.10 M and the average was taken. They may be expressed as a function of temperature by the equation

$$E = E_0 + ct + dt^2 \quad (4)$$

where E and E_0 are the normal electrode potentials of the mercury-mercurous sulfate electrode at temperatures t and 0° , respectively, and c and d are constants. The constants were obtained by the method of least squares and the equation with numerical values is

$$E = 0.63495 - 837.68 \times 10^{-6}t + 14.5 \times 10^{-9}t^2 \quad (5)$$

Experimental values are given in second column of Table II and those calculated from equation (5) in the fifth column. The value at 25° is much lower than the value calculated for this electrode by Lewis and Randall

Lewis and Randall, "Thermodynamics", McGraw-Hill Book Company, Inc., New York, 1923, pg. 407.

from the data of Randall and Cushman

Randall and Cushman, J. Am. Chem. Soc., 40, 393 (1918)

and an assumption as regards the activity coefficient of 0.0506 M at this temperature. The value is also lower than the value of Brodsky

Brodsky, Z. Electrochem., 35, 833 (1929)

obtained from solubility and potential data incorporated with the above data employed by Lewis and Randall.

In the third column of Table II, the E_0 values calculated by adding Δ values taken from the sixth column of Table V of the preceding paper to the E_0 values given in column 2 of Table II are given. The fifth column of Table II gives the E_0 's calculated from the equation

$$E_0 = 0.63495 - 787.54 \times 10^{-6}t - 23.92 \times 10^{-8}t^2 \quad (6)$$

The constants of this equation were obtained by the method of least squares. These latter E_0 's are higher than the former except at 0° but are still considerably lower than the reported values at 25° . Values obtained by the experimenters

Åkerlöf, J. Am. Chem. Soc., 48, 1160 (1926)
MacDougall and Blumer, *ibid.*, 55, 2236 (1933)

who employed the extended equation of Debye and Hückel are very much higher but must be in error due to the neglect of incomplete dissociation. These equations yield an ionic parameter of from 1.5 to 2.0 ångstrom units and is physically inconceivable and the ionic parameter probably changes with concentration.

The Stoichiometrical Activity Coefficients of Concentrated Sulfuric Acid Solutions: The values of the activity coefficients from 0.05 to 7.0 M are the same as those given in Tables VIII and IX of the preceding paper. The values calculated by the equation

$$E = E_0 - (3RT/2F) \ln m^{1/3} \quad (7)$$

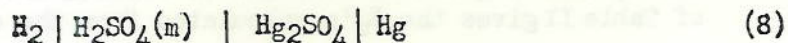
where E is the measured electromotive force at a molality, m, and E_0 is the normal electrode potential of the mercury-mercurous sulfate electrode, from 8.0 to 17.5 M, are given in Table III. These were calculated employing the E_0 values given in the second column of Table II. Those obtained by using the E_0 's given in the third column of Table II are given in Table IV. Both of these series are lower than those given by Lewis and Randall

Lewis and Randall, "Thermodynamics", McGraw-Hill Book Company, Inc., New York, 1923, pages 357 and 355.

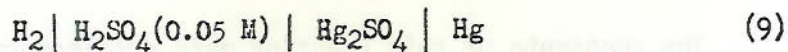
at 0 and 25°. It must be emphasized that these values as well as those given in the preceding paper are in constant ratio with Lewis and Randall's values except at higher concentrations where the ratio decreases indicating that the activity coefficient is lower than reported by them. This dropping off at higher concentrations was also observed by Vosburgh and Craig

Vosburgh and Craig, J. Am. Chem. Soc., 51, 2009 (1929)

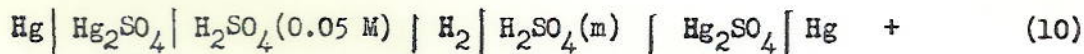
The Partial Molal Heat Contents of Sulfuric Acid Solutions Relative to 0.05 M Obtained from Measurements of $H_2|H_2SO_4(m)|Hg_2SO_4|Hg$ Cell: The partial molal heat contents of sulfuric acid were calculated relative to 0.05 M solution. Upon subtraction of the cell



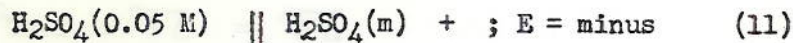
from the cell



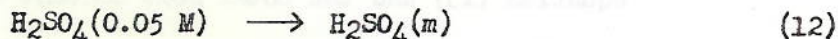
we obtain the cell



which is equivalent to the cell



Cell (11) corresponds to the reaction



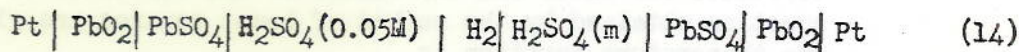
which is accompanied with an increase in free energy. The values of the electromotive forces and its temperature coefficient may be obtained from the data of Table I. If we substitute the temperature coefficient in the Gibbs-Helmholtz equation, as well as the corresponding partial free energy, we obtain the partial heat content of the acid relative to its value in 0.05 M sulfuric acid. These values were calculated at the thirteen temperatures and may be expressed as a function of temperature by the equation

$$\overline{\Delta H}(0.05 \text{ M}) = \overline{\Delta H}(0.05 \text{ M})_0 + \alpha t + \beta t^2 \quad (13)$$

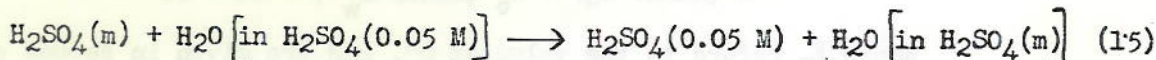
where the first term on the right is the value at 0° and α and β are constants. The latter two values were obtained by the method of least squares and values of $\overline{\Delta H}(0.05 \text{ M})_0$, α , and β are given in Table V.

The Partial Molal Heat Contents of Sulfuric Acid Solutions Relative to 0.05 M Obtained from Measurements of $\text{H}_2 \mid \text{H}_2\text{SO}_4(m) \mid \text{PbSO}_4 \mid \text{PbO}_2 \mid \text{Pt}$ Cell:

By the same steps as outlined above we obtain the cell



which corresponds to the reaction



This reaction is accompanied with a decrease in free energy when m is greater than 0.05 M, and is the reverse of cell (10) under the same conditions. Upon substitution of the temperature coefficient and corresponding partial free energy in the Gibbs-Helmholtz equation, we obtain the partial heat content of the acid relative to its value in 0.05 M sulfuric acid plus a quantity proportional to the logarithm of the ratio of the activities of water in the acid solutions also relative to 0.05 M sulfuric acid. The change in free energy corresponding to cell (14) is given by the equation

$$\overline{\Delta F}^c = \overline{F}_2 - \overline{F}_1 = -NE^cF = RT \ln (a_+^2, a_- / a_+^2 a_- a_w^2) \quad (16)$$

We desire, however, the quantity $\overline{\Delta F}^a$ which corresponds to the above reaction corrected for the water term, namely

$$\overline{\Delta F}^a = \overline{F}_2 - \overline{F}_1 = -NE^aF = RT \ln (a_+^2, a_- / a_+^2 a_-) \quad (17)$$

It follows from the temperature coefficient of $\overline{\Delta F}$ at constant pressure and the temperature coefficient of the electromotive force that

$$\overline{\Delta H}^a = \overline{\Delta H}^c + 2 RT^2 \, d \ln (a_w/a_w') / dT \quad (18)$$

which gives the relation between the total heat content corresponding to equation (15) and the total heat content corresponding to equation (12).

The former quantities are obtained directly from the data given in Table IV of the preceding paper. The values of $\overline{\Delta H}^c$ or the cell values relative to 0.05 M acid are given in Table VI. These were calculated at the thirteen temperatures and may be expressed as a function of temperature by the equation

$$\overline{\Delta H}^c (0.05 \text{ M}) = \overline{\Delta H}^c (0.05 \text{ M})_0 + \lambda t + \int t^2 \quad (19)$$

The constants λ and \int were obtained by the method of least squares and values of $\overline{\Delta H}^c (0.05 \text{ M})_0$, λ and \int are given in the second, third and fourth columns of Table VI. Only values at 0° are given.

In order to obtain $\overline{\Delta H}^a$ relative to 0.05 M acid we have corrected the electromotive forces given in Table IV of preceding paper for the activity of water. The method of calculating the activity of water was described on page 18 of preceding paper. The term $(RT/F) \ln a_w$ was evaluated and subtracted from the electromotive forces given in Table IV of preceding paper. The values of the electromotive forces corrected for water and the values of the constants of the temperature equation obtained by the method of least squares are given in Table VII. The temperature equation is

$$E (\text{minus } a_w) = E_0 (\text{minus } a_w) + et + ft^2 \quad (20)$$

where E_0 refers to the value at 0°, and are given in second column of Table VII. These values were employed to calculate the partial molal heat contents of the acid relative to 0.05 M sulfuric acid. They are by necessity the same as those given in Table V, since the water corrections were obtained by differences of the cells not involving and involving the water term. The differences of the values in Tables V and VI give the values of the quantity $2RT^2 \, d \ln (a_w/a_w') / dT$ relative to 0.05 M. We have not listed these values. Suffice it to say that they are related to \overline{L}_1 . It should be pointed out here that the relative partial molal heat contents relative to 0.05 M sulfuric acid obtained from the mercurous sulfate cell differ in sign from those obtained from the lead dioxide cell under the same conditions since one proceeds with an increase in free energy and the other with a decrease.

The Partial Molal Heat Contents of Sulfuric Acid Solutions Relative to Infinite Dilution: Above we have calculated the heat contents relative to 0.05 M sulfuric acid. The same quantities relative to infinite dilution (\overline{L}_2) are desired. These may be calculated from the equation

$$\overline{L}_2 = -r RT^2 \, d \ln f/dT \quad (20)$$

Since the expression for the activity coefficient has not been clearly defined we have resorted to an extrapolation to obtain \bar{L}_2 . In Fig. 1 we have plotted ΔH against the square root of the molality. The plot shows a slight curvature in dilute solutions making an extrapolation difficult. As an aid in the extrapolation we have taken a value of \bar{L}_2 at 0.005 m from Lange, Monheim and Robinson's

Lange, Monheim and Robinson, J. Am. Chem. Soc., 55, 4733 (1933)

paper and calculated the value which the extrapolation should be to be consistent with their data. The dotted line in Fig. 1 is drawn to this value and it will be noticed that the last few experimental points fall on a straight line. This extrapolation is also consistent with the E_0 values obtained by the Lewis and Linhart straight line function minus the "hump". The extrapolated value is then added to each of the $\Delta H(0.05 m)$ in order to obtain \bar{L}_2 . These are given at 0° in second column of Table VIII. They may be expressed as a function of temperature by the quadratic equation

$$\bar{L}_2 = \bar{L}_2^0 + \alpha' t + \beta' t^2 \quad (21)$$

Since the extrapolated value is taken the same at all temperatures, the constants α' and β' would be the same as the constants α and β for equation (13). A refinement may be made by taking the temperature coefficient of ΔH at 0.05 m and correcting the others or the \bar{L}_2 's for this. However, this temperature coefficient is so small as to make such a correction meaningless. In view of this α' and β' are taken equal to α and β and consequently are not given in Table VIII. In Fig. 2 we have plotted \bar{L}_2 against the square root of the molality. The unshaded circles are the experimental values, the shaded ones those of Lange, Monheim and Robinson, and the squares are those of Brønsted

Brønsted, Z. physik. Chem., 68, 693 (1910)

See also Lewis and Randall, "Thermodynamics", McGraw-Hill Book Co., Inc., New York, 1923, page 95.

Brønsted's data ~~were~~ found to be approximately 3000 calories lower than ours and this value has been added to all of Brønsted's data before ~~they were~~ plotted. Our values are in very close check with Lange, Monheim and Robinson's data in the limited range in which a comparison may be made. Our values become less than theirs as the concentration increases and deviates about 200 calories at 0.04 m . The low values of Brønsted are probably due to the method of extrapolation which he employed. Since our values are in constant ratio with his this seems to be evident.

However, if the E_0 's given in the third column of Tables V of the preceding paper and 2_0 of this paper are taken as correct the plot of $\Delta H(0.05 M)$ against the square root of the molality will not approach infinite dilution linearly but will curve in dilute solutions, and approach the limiting law. This curve will occur however at molalities too dilute to be experimentally verified. To determine the magnitude of this difference, we have calculated \bar{L}_2 from equation (20) at 0.0005M employing first the activity coefficient given in Table VIII of preceding paper. This value checks the value given in Table VIII for \bar{L}_2 and shows that the extrapolation using the linear relation is consistent with the E_0 's given in column 2 of Table II and Table V of preceding paper. Secondly, we employed the activity coefficient given in Table IX of preceding paper and obtained a value 456 calories lower. In Fig. 1 the dotted line corresponds to this value. The straight line extrapolation gives 4883 calories at infinite dilution and the curve 4427 calories. The limiting slope is labeled "L.L." and the curve from foregoing relations must approach it. The \bar{L}_2 's given in Table VIII may be converted for this latter extrapolation by subtracting 456 calories, from all the values at the various molalities.

The Relative Partial Molal Specific Heat: - The differentiation of equation with respect to temperature was employed to evaluate the relative partial molal specific heat. This gives equation

$$d \bar{L}_2 / dT = \overline{\Delta C_p} = \alpha' + 2 \beta' t \quad (22)$$

and second differentiation gives the equation

$$d \overline{\Delta C_p} / dT = 2 \beta' \quad (23)$$

from which $\overline{\Delta C_p}$ and its variation with temperature can be obtained readily by employing the constants in Table V. Harned and Ehlers

Harned and Ehlers, J. Am. Chem. Soc., 55, 2179 (1933)

stated that if it is necessary to employ a constant b (or a t^2 term) in the expression of the electromotive forces as a function of temperature, then the relative partial molal specific heat has a temperature coefficient. This is only strictly true if b is a function of concentration. If b remains the same at all concentrations then $\overline{\Delta C_p}$ has no coefficient, or if b varies but slightly the temperature coefficient is very small. Sulfuric acid approaches these conditions. In Table IX we have given the values of $\overline{\Delta C_p}$ at zero degrees and the values of $2 \beta'$. It will be noticed that the latter are exceedingly small.

Summary

- (1) Measurements are given for the cell $H_2 | H_2SO_4(m) | Hg_2SO_4 | Hg$ from 0.05 to 17.5 M and over the temperature range of from 0 to 60°.