

Review

The electromotive force of the lead–acid cell and its half-cell potentials

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Abstract

The literature values of the activity coefficients of sulfuric acid, and the activities of water as a function of the molality of aqueous sulfuric acid and temperature, are reviewed and evaluated. Approaches to fitting these values to a suitable equation are also reviewed. A self-consistent set of values for acid and water activities and the standard potentials of the lead–acid cell and mercurous sulfate–mercury electrode are identified. These values are used to calculate the electromotive force (e.m.f.) of the lead–acid cell from 0.1 to 30 m H_2SO_4 . Temperature coefficients for the e.m.f. are also available from 0 to 60 °C. Accurate half-cell potentials versus a mercurous sulfate–mercury electrode can be calculated for molalities from 0.1 to 7.2 and for temperatures from 0 to 55 °C.

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1. Introduction

1.1. Purpose

The open circuit voltage of the lead–acid cell can vary from over 2 to 0 V, depending on the acid concentration and temperature. Because open circuit voltage is an inexpensive and non-destructive measurement, it is frequently interpreted as an indicator of either the state of charge or the state of health of the cell or battery. Such interpretations can be misleading, however, unless the cell has reached a true state of equilibrium, and this frequently takes at least one day. The open circuit voltage of a cell which has just been charged or discharged, or is freshly formed, can vary significantly from its equilibrium potential or electromotive force (e.m.f.). This variation is caused by concentration and temperature gradients within the separator and porous electrode, acid stratification from top to bottom, and formation of transient chemical species such as lead persulfate at the end of charge.

Despite these hazards, the open circuit voltage can give important information about the state of the lead-acid cell and its reactions. The literature contains approximately 50 publications on the activities of the sulfuric acid and the free energies of the cell reactions as a function of acid concentration and temperature. It is the purpose of this paper to review and evaluate this literature and recommend a consistent set of values for acid and water activities, and for the standard potentials of the lead–acid cell as well as its half-cell potentials versus a mercurous sulfate–mercury electrode.

1.2. Background

The electromotive force (e.m.f.) of the lead–acid battery is a function of the acid concentration and temperature. The Nernst equation can be used to calculate the e.m.f. for a given acid molality and temperature if the mean ionic activity coefficient of sulfuric acid, the activity of water, and the standard potential of the cell reaction are known. Since the activities of aqueous sulfuric acid can be determined from vapor pressure and freezing point measurements as well as from the electromotive forces of various cells, they can be used to evaluate and extend the literature values of the e.m.f. of the lead–acid battery. This paper will review the literature on the activity coefficients of sulfuric acid, the activities of water, and the electrode potentials for the positive and negative electrodes of the lead–acid battery and the mercurous sulfate–mercury reference electrode. Based on the best data available, e.m.f.s. can be calculated for a broad range of acid concentrations and temperatures.

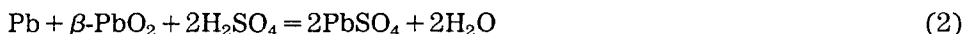
The use of an 'effective thermodynamic concentration', or 'activity' to resolve the discrepancies between the thermodynamic properties of electrolytes at finite concentrations and the predictions of the laws of ideal solutions at infinite dilution [1] was proposed by Lewis in 1907. He stated that the activity of any dissolved substance, α , is related to the free energy, G , by the equation

$$dG = RT \ln \alpha \quad (1)$$

This formula is the basis for the use of activities instead of concentrations in the Nernst equation, which relates the electromotive force of an electrochemical cell to the temperature and the concentrations of the reactants and products in the cell reaction.

1.3. Nernst equation and activities in lead-acid cells

For a lead-acid cell, the Nernst equation is based on the double sulfate reaction



and the electromotive force (e.m.f.)

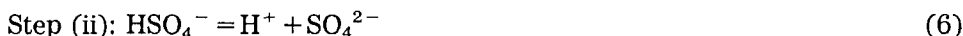
$$E = E^\circ + (RT/F)(\ln a_{\text{H}_2\text{SO}_4} - \ln a_{\text{H}_2\text{O}}) \quad (3)$$

Thus the activities of sulfuric acid and water must be known at any given concentration or temperature in order to calculate the e.m.f. of the lead-acid cell using this equation.

Sulfuric acid is a uni-bivalent electrolyte which dissociates in water in two steps according to the following equilibria:



$$\text{where } K_1 = \frac{[a_{\text{H}^+}][a_{\text{HSO}_4^-}]}{[a_{\text{H}_2\text{SO}_4}]} \quad (5)$$



$$\text{where } K_2 = \frac{[a_{\text{H}^+}][a_{\text{SO}_4^{2-}}]}{[a_{\text{HSO}_4^-}]} \quad (7)$$

where a refers to the activities of the designated ions in solution and K_1 and K_2 are the equilibrium constants for the two dissociation steps.

K_1 is infinity because dissociation of aqueous sulfuric acid into hydrogen and bisulfate ions is essentially complete, whereas K_2 is about 10^{-2} . Thus, sulfuric acid is only partially dissociated and contains a complex mixture of hydrated hydrogen, bisulfate, and sulfate ions that varies with concentration and temperature.

The activity of any ion

$$a = \gamma m \quad (8)$$

Because it is not possible to measure individual ionic activities, a mean ionic activity coefficient, γ_{\pm} , is used to define the activities of all ions in a solution.

The convention used in the literature to report the mean ionic activity coefficients for sulfuric acid is based on the assumption that the acid dissociates completely into hydrogen and sulfate ions. This assumption leads to the following relationships between the activities, activity coefficients, and molalities of the sulfuric acid and its ions.

$$[a_{\text{H}_2\text{SO}_4}] = [(a_{\text{H}^+})^2][a_{\text{SO}_4^{2-}}] = (\gamma_{\pm} 2m)^2 (\gamma_{\pm} m) = 4\gamma_{\pm}^3 m^3 \quad (9)$$

where m is the molality of the sulfuric acid (moles acid/kg water).

Assuming complete dissociation of sulfuric acid into three ions, the activity of water is given by the following formula:

$$\ln a_{\text{H}_2\text{O}} = -\nu m \phi \frac{M_{\text{H}_2\text{O}}}{1000} = -3m\phi/55.5 \quad (10)$$

The activity coefficients of sulfuric acid may be determined independently by measuring three types of physical phenomena: electromotive force, vapor pressure and freezing point. The literature contains a large number of such measurements and calculated values for the activity of water and the activity coefficients of sulfuric acid based upon them [2–41].

The approach used in the following data analysis is as follows:

(i) the activity coefficients for sulfuric acid reported in the literature are compared to determine the values which, based on independent methods of measurement, agree with one another;

(ii) the best activity coefficients found are then used to evaluate the best values to use for the standard potentials of the half-cell reactions in the lead–acid battery. These standard potentials must be consistent with the activity coefficients in order to calculate an accurate cell potential;

(iii) the e.m.f.s of the lead–acid cell at 25 °C are calculated as a function of acid concentration from 0.1 to 30 m using the Nernst equation and the best values for the activity coefficients of sulfuric acid obtained from vapor pressure measurements, the activities of water, and the standard cell potential. These calculated values agree closely with values obtained from cell measurements which are available up to about 7 molal;

(iv) temperature coefficients for the e.m.f. of the lead–acid cell, which were determined from heat capacity measurements of the cell reactants and products using the third law of thermodynamics, are used to correct the e.m.f. for temperature up to 13.877 m acid;

(v) measured potentials for the lead sulfate, lead dioxide, and mercurous sulfate–mercury reference electrode versus the hydrogen electrode in the same acid concentration are used to calculate the half-cell potentials of the positive electrode in the lead–acid battery.

By using this approach, e.m.f. data for the lead–acid cell can be calculated for acid molalities from 0.1 to 30 and temperatures from 0 to 60 °C. The half-cell potentials of the positive and negative electrodes versus a mercurous sulfate–mercury reference electrode can be calculated for acid molalities from 0.1 to 7.2 and at temperatures from 5 to 55 °C.

The following cells will be referred to in the text by number:

Cell I. (Pt)H₂|H₂SO₄(m)|PbSO₄|β-PbO₂(Pt)

Cell II. (Pt)H₂|H₂SO₄(m)|Hg₂SO₄(Hg)

Cell III. Pb(Hg)|PbSO₄|H₂SO₄(m)|H₂(Pt)

Cell IV. Pb|Pb²⁺|Pb(Hg)

Cell V. Hg|Hg₂SO₄|H₂SO₄(m)|PbSO₄|β-PbO₂(Pt)

2. Literature survey of the activities of sulfuric acid and water

2.1. Activities of sulfuric acid and water

In 1919, Lewis and Linhart [2] calculated activity coefficients for very dilute concentrations of sulfuric acid, 10^{-7} to 10^{-2} m, from the freezing-point data of Hausrath [3]. Apparently no other authors have reported activity coefficients below 10^{-4} m. Two years later, Lewis and Randall [4] discussed different methods of determining activity coefficients using vapor pressure, freezing point, and electromotive force measurement techniques. They calculated activity coefficients for sulfuric acid at 25 °C based on each of these methods, using vapor pressures from Bronsted [5], freezing points from Drucker [6], Roth and Knothe [7], and Pickering and Barnes [8], and electromotive force data for Cell II from Randall and Cushman [9]. Because the agreement between these independently determined values was good, they reported a set of composite values for 0.01–10 m. Harned and Akerlof [10] also calculated activity coefficients from the e.m.f. data of Randall and Cushman [9]. Randall and Scott [11] subsequently obtained freezing point data for sulfuric acid solutions in the 10^{-3} – 10^{-1} m range, averaged them with Hausrath's data, and published a new set of activity coefficients. Grollman and Frazer [12] and MacDougall and Blumer [13] used their own vapor pressure measurements to determine activity coefficients for sulfuric acid from 0.073 to 2.871 m and from 0.056 to 2.5 m, respectively, at 25 °C. MacDougall and Blumer also determined activity coefficients in the same range from measurements of the e.m.f. of Cell II.

Vosburgh and Craig [14] obtained activity coefficients for 0.05–3.5 m from measurements of the e.m.f. of Cell V. Use of e.m.f. measurements of the Hg_2SO_4 –Hg electrode to determine the activity coefficients of sulfuric acid is subject to an error at concentrations below about 0.005 m, due to the sparing solubility of Hg_2SO_4 in H_2SO_4 . To avoid this problem, Baumstark [15] and Shrawder and Cowperthwaite [16] determined activity coefficients from e.m.f. measurements of Cell III at sulfuric acid concentrations from 10^{-3} to 2×10^{-2} m and at temperatures of 0, 12.5, 25, 37.5 and 50 °C. They considered that the solubility of lead sulfate in this concentration range is too low to necessitate a correction for the concentration of soluble lead sulfate. Lilley and Briggs [17] later recalculated activity coefficients from Shrawder and Cowperthwaite's data using a more accurate value for the standard electrode potential of the PbSO_4 , Pb(Hg) electrode at 25 °C and corrected for the solubility of lead sulfate. Lilley and Briggs did not specify the solubilities of lead sulfate which were used in their calculation.

Hamer [18] and Harned and Hamer [19], based on measurements of Cells I and II, respectively, calculated activity coefficients for 5×10^{-4} –17.5 m sulfuric acid at 0, 15, 25, 40 and 60 °C. Subsequently, Scatchard *et al.* [20] used vapor pressure measurements to determine activity coefficients from 0.1 to 4 m. Shankman and Gordon [21] used vapor pressure measurements to determine activity coefficients from 1 to 16 m. They were apparently the first of many authors to point out that the cell measurements of Harned

[19] are not very accurate, but they noted that the values of Scatchard *et al.* [20] were in satisfactory agreement. Robinson [22] reported that activity coefficients calculated from the vapor pressure measurements agreed with those of Scatchard *et al.* with a mean deviation of 0.2% of the activity coefficient, assuming the same reference activity coefficient value of 0.209 at $m=0.2$. This value is based on a K_2 of 0.0120. Robinson noted, however, the problems associated with assuming a reference value, and reported a second set of coefficients based on a different reference value which agreed more closely with Harned and Hamer [19].

Based on their e.m.f. data, Harned and Hamer [19] reported the activity of water from 5×10^{-4} to 17.5 m H_2SO_4 at 0, 25, 40, and 60 °C. Stokes [23] later recalculated the water activities at 25 °C from the data of Harned and Hamer [18, 19]. In 1939, Shankman and Gordon [21] and Sheffer *et al.* [24] gave the activities of water from 0.16 to 0.69 m and from 0.05 to 4 m sulfuric acid, respectively, at 25 °C. The same year, Robinson [22] determined water activities from 1.2 to 1.8 m at 25 °C from the data of Grollman and Frazer [12]. Stokes [25] gave water activities in 3–11.5 m sulfuric acid solutions at 25 °C, and Robinson and Stokes [26] tabulated activities from 0.1 to 76 m.

In 1959, Beck *et al.* [27] reported activities of water from 0.1 to 8.3 m based on measurements of Cell I. The same year, Giaque *et al.* [28] published a compilation of the heat capacities, entropies, free energies, and heat contents for the $\text{H}_2\text{SO}_4\text{--H}_2\text{O}$ system, most of which had been measured by Giaque and coworkers [28]. Based on these data, they calculated the activities of water and the activity coefficients for sulfuric acid at 25 °C from 1 to 1000 m. The values of the activity of water given by Stokes *et al.*, and Giaque *et al.*, agree within 3 significant figures and are therefore recommended. Harned and Hamer's activities at 25 °C agree to within 2 significant figures. Their values at 0, 40 and 60 °C are probably the only ones in the literature. Deno and Taft [29] determined the activity of H_2O for 50–95% H_2SO_4 , which is outside the typical range of 0–40% used in the lead–acid cell.

In 1956, Glueckauf and Kitt [30] used vapor pressure measurements to determine the activity coefficients of sulfuric acid from 0 to 76 m at 25 °C. They corrected their vapor pressures by an unexplained factor of 0.08 to make them agree with previously published vapor pressure data. This work does not appear to be very accurate.

Covington *et al.* [31] have obtained probably the most accurate activity coefficients for sulfuric acid from 0.1 to 8 m at 25 °C. They used the remeasured e.m.f. values of Beck *et al.* [27, 32] on the two types of cells measured by Hamer [18] and Harned and Hamer [19] (Cells I and II). Covington *et al.* found close agreement in the activity coefficients determined from the e.m.f. measurements of the two cell types. They also recalculated the activity coefficients tabulated by Robinson and Stokes [26] from the vapor pressure data of Stokes [33], which were originally calculated using Hamer's data, and found agreement with their measurements. Lilley and

Briggs [17] calculated activity coefficients for 0.01 and 0.02 m from Covington's data and showed that these values agree with the recalculated data of Shrawder and Cowperthwaite. Gardner *et al.* [34] used a third-law method to extend the range of activity coefficients determined from Cells I and II to temperatures from 5 to 55 °C using the data of Wynne-Jones *et al.* [27, 32] and their own measurements of the partial molal heat capacities of sulfuric acid. Their values agree with Covington *et al.* at 25 °C.

Wirth [35], using the data of Covington *et al.* [31] compared the activity coefficients of sulfuric acid at 25 °C assuming values for K_2 of 0.0102 and 0.0104. He recommended Covington's value of 0.0102 for K_2 .

3. Fitting equations

Pitzer has developed a system of equations for the thermodynamic properties of electrolytes up to 6 molal based on the Debye–Huckel model [36]. These equations include a term for the effect of short-range forces between ions, and a term for triple ion interactions. Pitzer *et al.* recalculated [37] the activity coefficients for 0.01 m at 0, 12.5, 25, 37.5, and 50 °C from the data of Shrawder and Cowperthwaite [16] and developed [38] the coefficients for the equations for the thermodynamic properties of sulfuric acid as a function of temperature. The activity coefficients which Pitzer *et al.* [38] obtained for sulfuric acid concentrations from 0.1 to 6.0 m at 25 °C using a K_2 value of 0.0105 are in good agreement with the values of Covington *et al.* [31], and his water activities agree closely with those of Robinson and Stokes [26] and Giauque *et al.* [28].

Pitzer's equations [38] can be used to calculate the activities of sulfuric acid as a function of acid concentration and temperature. The equations can also be used to calculate the osmotic coefficients of sulfuric acid and therefore the activities of water as a function of acid concentration and temperature. Also of interest is the fact that Pitzer's equations can be used to calculate the standard electrode potentials of Cells I, II, and III. Cell III is related to the potential of the negative electrode in the lead–acid battery versus the hydrogen electrode. However, the potential of Cell III must be corrected by adding the potential for Cell IV, $E = 0.0057 + 0.000\ 016 (t - 25)$, where t is the temperature in °C, to get the standard potential of the negative electrode [14, 39].

Rard *et al.* [40] reviewed the literature on vapor pressures and osmotic coefficients of sulfuric acid at 25 °C. They used the Debye–Huckel limiting law with an additional power series to calculate the activity coefficients. Their values agree with Covington *et al.* [31] to within 1%. Both the osmotic and activity coefficients published by Rard and Pitzer also agree within 1%. The water activities published by Rard *et al.* agree within 1% with those of Robinson and Stokes [26] and Giauque *et al.* [28].

In 1981, Staples [41], of the United States National Bureau of Standards, published recommended values for the activity coefficients of sulfuric acid

and the activities of water at 25 °C for 0.001–27.5 m H₂SO₄. Staples first did a very thorough compilation of the original literature on e.m.f., vapor pressure and freezing point measurements. He concluded that the e.m.f. values gave the most consistent data and used these to calculate activity coefficients. His recommended values were obtained by a linear regression analysis based on an empirical equation which did not include the Debye–Huckel limiting law. Staples' activity coefficients for H₂SO₄ agree within 2% with the results of Covington *et al.* [31] and Pitzer *et al.* [38]. Staples noted that the agreement of his recommended values with those calculated using the equations of Pitzer *et al.* is 'within any experimental uncertainty'. The water activities recommended by Staples in general agree, within 1%, with those of Robinson and Stokes [26].

4. Electromotive force of the lead–acid cell and its half-cell potentials

4.1. *E.m.f.s of lead–acid cells*

The agreement discussed previously in the literature between the activity coefficients determined using Cells I, II and III and vapor pressure measurements suggests that accurate values for the open circuit voltages of the lead–acid cell may be calculated up to 30 m using the Nernst equation for the double sulfate reaction. At higher concentrations, the solubility of lead sulfate increases rapidly and the Nernst equation for the cell reaction may need to be modified [42]. However, higher values have little practical value, because the concentration of sulfuric acid in the lead–acid cell is still limited to about 8 m by other considerations, such as cycle life and acid conductivity.

Table 1 shows the results of this calculation at 25 °C. Column 0 is the molality of sulfuric acid. The values for the activity coefficients of sulfuric acid are given in Column 1. These values were determined by correcting the values given by Robinson and Stokes [26] to reference them to the same activity coefficient value as the data of Covington *et al.* [31], $\gamma_{0.1\text{ m}} = 0.245$. The formula used to make this correction, derived from the Gibbs–Duhem equation [31], is $\ln \gamma_1 = \ln(0.245/0.2655) + \ln \gamma_2$, where γ_1 is the corrected value.

The values of the activity of water given in Column 2 of the Table are also from Robinson and Stokes [26]. Column 3 of Table 1 and Fig. 1 show the activity of sulfuric acid calculated using the values in Columns 0 and 1.

The electromotive force of the lead–acid cell is shown in Column 4 and Fig. 2. Figure 3 shows the e.m.f. as a function of acid activity. The following standard cell potentials were used in the calculation. 1.690 V for Cell I from Covington *et al.* [31], –0.3526 V for Cell III from Lilley and Briggs [17] and 0.0057 V for Cell IV from Gerke [39]. The value of 1.690 V for Cell I is also recommended in the IUPAC study [43]. The value of –0.3505 V for Cell III recommended by IUPAC is based on the data of Shrawder and

TABLE 1

Thermodynamic values for the lead-acid cell at 25 °C

Molality	1 Gamma	2 a Water	3 a Acid	4 E.M.F.
0.1	0.245	9.963×10^{-1}	5.882×10^{-5}	1.798
0.2	0.193	9.928×10^{-1}	2.296×10^{-4}	1.833
0.3	0.169	9.892×10^{-1}	5.167×10^{-4}	1.854
0.5	0.144	9.819×10^{-1}	1.483×10^{-3}	1.881
0.7	0.131	9.743×10^{-1}	3.067×10^{-3}	1.900
1.0	0.121	9.618×10^{-1}	7.164×10^{-3}	1.922
1.5	0.117	9.387×10^{-1}	2.137×10^{-2}	1.951
2.0	0.118	9.126×10^{-1}	5.224×10^{-2}	1.975
2.5	0.123	8.836×10^{-1}	1.158×10^{-1}	1.996
3.0	0.131	8.516×10^{-1}	2.440×10^{-1}	2.016
3.5	0.143	8.166×10^{-1}	4.989×10^{-1}	2.035
4.0	0.157	7.799×10^{-1}	9.883×10^{-1}	2.054
4.5	0.173	7.422×10^{-1}	1.888×10^0	2.072
5.0	0.192	7.032×10^{-1}	3.541×10^0	2.090
5.5	0.213	6.643×10^{-1}	6.463×10^0	2.106
6.0	0.237	6.259×10^{-1}	1.148×10^1	2.123
6.5	0.263	5.879×10^{-1}	2.002×10^1	2.139
7.0	0.292	5.509×10^{-1}	3.421×10^1	2.154
7.5	0.323	5.152×10^{-1}	5.685×10^1	2.169
8.0	0.356	4.814×10^{-1}	9.255×10^1	2.183
8.5	0.393	4.488×10^{-1}	1.492×10^2	2.197
9.0	0.431	4.180×10^{-1}	2.334×10^2	2.211
9.5	0.472	3.886×10^{-1}	3.617×10^2	2.224
10.0	0.516	3.612×10^{-1}	5.490×10^2	2.236
11.0	0.610	3.111×10^{-1}	1.208×10^3	2.260
12.0	0.711	2.681×10^{-1}	2.480×10^3	2.283
13.0	0.819	2.306×10^{-1}	4.835×10^3	2.304
14.0	0.938	1.980×10^{-1}	9.072×10^3	2.324
15.0	1.065	1.698×10^{-1}	1.630×10^4	2.343
16.0	1.200	1.456×10^{-1}	2.828×10^4	2.361
17.0	1.338	1.252×10^{-1}	4.708×10^4	2.378
18.0	1.484	1.076×10^{-1}	7.621×10^4	2.394
19.0	1.634	9.250×10^{-2}	1.198×10^5	2.410
20.0	1.790	7.960×10^{-2}	1.836×10^5	2.424
21.0	1.951	6.860×10^{-2}	2.750×10^5	2.439
22.0	2.122	5.890×10^{-2}	4.072×10^5	2.453
23.0	2.302	5.060×10^{-2}	5.940×10^5	2.466
24.0	2.460	4.410×10^{-2}	8.233×10^5	2.478
26.0	2.805	3.310×10^{-2}	1.552×10^6	2.502
28.0	3.159	2.500×10^{-2}	2.767×10^6	2.524
30.0	3.499	1.910×10^{-2}	4.627×10^6	2.544
32.0	3.831	1.472×10^{-2}	7.372×10^6	
34.0	4.146	1.148×10^{-2}	1.120×10^7	
36.0	4.455	9.000×10^{-3}	1.650×10^7	
38.0	4.748	7.110×10^{-3}	2.349×10^7	
40.0	4.989	5.750×10^{-3}	3.178×10^7	
42.0	5.219	4.670×10^{-3}	4.213×10^7	
44.0	5.436	3.810×10^{-3}	5.474×10^7	
46.0	5.626	3.150×10^{-3}	6.934×10^7	

(continued)

TABLE 1 (continued)

Molality	1 Gamma	2 a Water	3 a Acid	4 E.M.F.
48.0	5.793	2.620×10^{-3}	8.601×10^7	
50.0	5.946	2.200×10^{-3}	1.051×10^8	
52.0	6.077	1.855×10^{-3}	1.263×10^8	
54.0	6.183	1.585×10^{-3}	1.489×10^8	
56.0	6.291	1.355×10^{-3}	1.749×10^8	
58.0	6.373	1.168×10^{-3}	2.020×10^8	
60.0	6.443	1.010×10^{-3}	2.311×10^8	
62.0	6.501	8.820×10^{-4}	2.619×10^8	
64.0	6.543	7.740×10^{-4}	2.938×10^8	
66.0	6.575	6.840×10^{-4}	3.269×10^8	
68.0	6.601	6.060×10^{-4}	3.617×10^8	
70.0	6.617	5.370×10^{-4}	3.976×10^8	
72.0	6.627	4.800×10^{-4}	4.344×10^8	
74.0	6.629	4.300×10^{-4}	4.722×10^8	
76.0	6.627	3.870×10^{-4}	5.111×10^8	

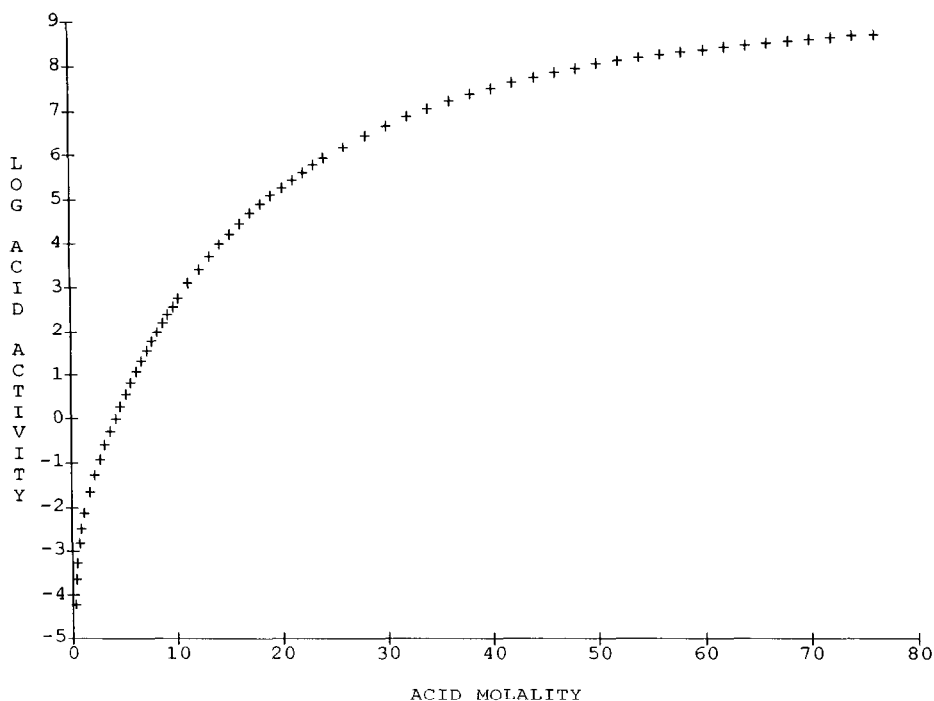


Fig. 1. The activity of aqueous sulfuric acid as a function of acid molality at 25 °C.

Cowperthwaite [16] using a $K_2=0.0120$ rather than the apparently more accurate value of Lilley and Briggs [17], who re-evaluated the same data using a $K_2=0.0104$. Pitzer [37] has recommended a value of -0.3513 V using a $K_2=0.0125$. Pitzer's value was calculated using a Debye-Huckel

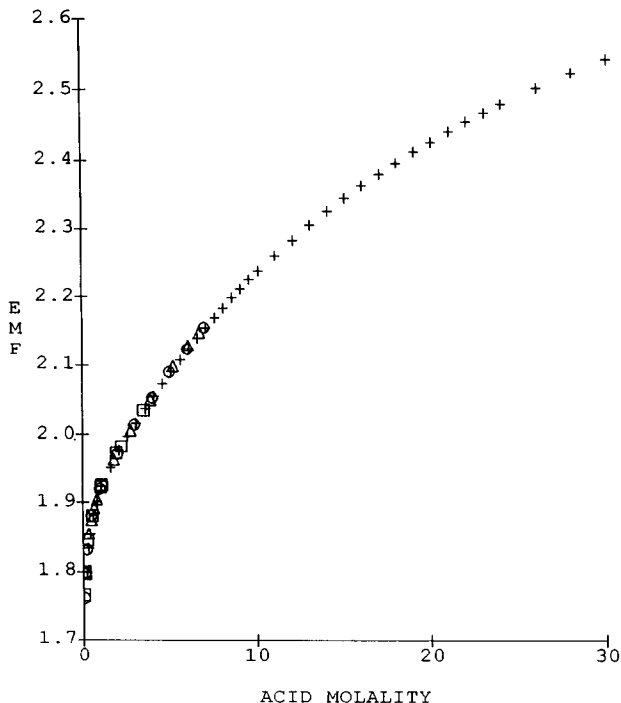


Fig. 2. The electromotive force of the lead-acid cell as a function of acid molality at 25 °C. +, Nernst equation; O, Harned, Hamer [44]; Δ, Craig, Vinal [43]; □, Vosburgh, Craig [14].

function which included the limiting law and the data of Shrawder and Cowperthwaite. The values of the constants used to calculate these values were $R = 8.314\ 41\ \text{J mol}^{-1}\ \text{T}^{-1}$; $F = 9.648\ 456 \times 10^4\ \text{C eq}^{-1}$ and $T = 298.15\ \text{K}$ [43].

The sum of the standard potentials for Cells I, III and IV gives a standard potential for the lead-acid cell of 2.048 V at 25 °C. This value was rounded to the nearest millivolt due to the uncertainties inherent in its determination. Covington *et al.* [31] have estimated that the uncertainty in the standard potential of Cell I is at least 0.30 mV, depending on the choice of the adjustable parameters in the Debye-Huckel equation and the value of K_2 used, and Pitzer [37] has estimated the same uncertainty for the standard potential of Cell III.

As shown in Fig. 2, the calculated e.m.f. values agree within several millivolts with the measurements reported by Craig and Vinal [44] on lead-acid cells, as well as with the data calculated from cell measurements by Vosburgh and Craig [14] and Harned and Hamer [45]. They also agree with the values calculated by Duisman and Giauque [46] up to 13.877 m. This agreement gives credence to the higher calculated values and establishes once again the validity of the double sulfate reaction for the lead-acid battery.

In a recent study of standard potentials published by the International Union of Pure and Applied Chemistry [43], the values for the electromotive

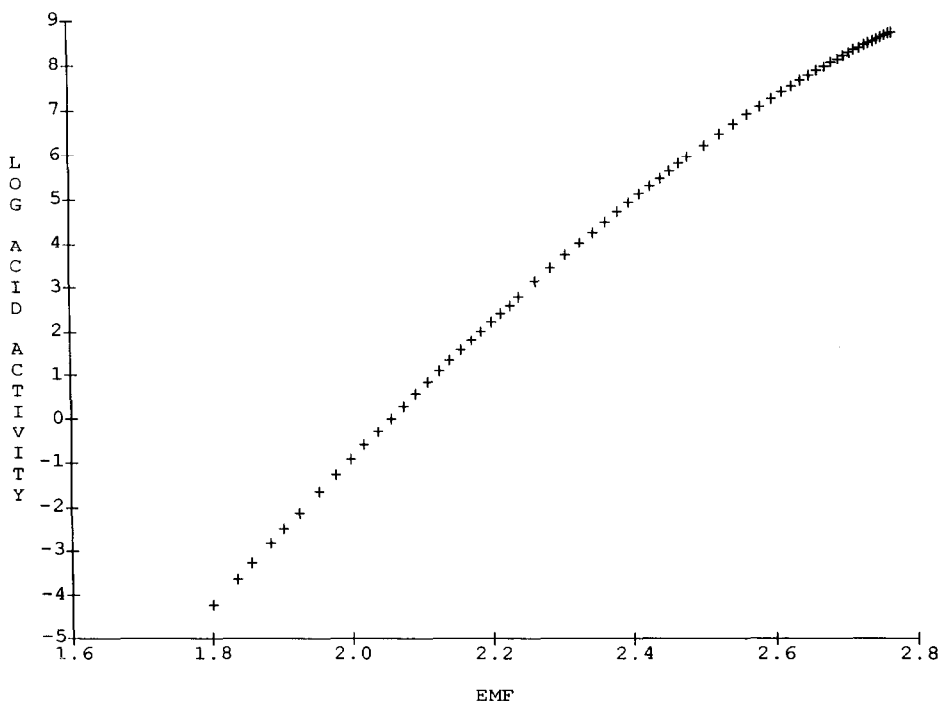


Fig. 3. The activity of aqueous sulfuric acid in a lead-acid cell as a function of the cell e.m.f. at 25 °C.

force of the lead-acid battery originally given by Harned and Hamer [45] for molalities from 0.05 to 7.0 m were republished without critical comment. In an earlier review, Craig and Vinal [44] found that the e.m.f. values of Harned and Hamer [45] agreed within several millivolts with their measurements of lead-acid cells at 25 °C, as did the values calculated by Vosburgh and Craig [14]. The more recently calculated e.m.f.s of Duisman and Giaouque [46] also agree with these authors.

The e.m.f. values of Harned and Hamer were calculated using their measured e.m.f.s. of Cells I, II [18, 19] as well as other cell data. Although inaccuracies in these cell measurements have frequently been pointed out, they do not seem to be reflected in the final e.m.f. values at 25 °C. Some of these errors may be cancelling in the calculation.

The measured values of Craig and Vinal [44] are higher than earlier values measured on lead-acid cells. They used a lead-calcium alloy for the current collectors in their cells and suggested that the use of lead-antimony alloys in the early cell measurements may have accelerated dilution of the acid in the electrodes by self-discharge reactions.

This is only one of several problems encountered in direct e.m.f. measurements of the lead-acid cell. Duisman and Giaouque [46] have suggested that the e.m.f. of Cell I may vary with the method of preparation used for the β - PbO_2 , since it is not entirely stoichiometric. In addition, pasted battery

plates generally contain some α -PbO₂, which has a standard electrode potential in sulfuric acid about 8 mV higher than β -PbO₂ [43]. If the pasted plate is not well formed, it may also contain lead monoxide, which self-discharges rapidly. Another problem is that overcharge can produce other compounds, such as persulfate, which can affect the potential.

4.2. Half cell potentials

The mercurous sulfate–mercury electrode is frequently used as the reference electrode in studying the half-cell reactions in the lead–acid battery. The standard potential for Cell II of 0.6125 V from Covington *et al.* [31] appears to be a good value. This value was also recommended by Gardner *et al.* [34] and is consistent with the activity coefficients and standard potentials used to calculate the lead–acid cell e.m.f.s in Table 1. Brackett *et al.* [47], using heat capacity measurements, have shown that the earlier e.m.f. measurements for Cell II reported by Harned and Hamer [19] are in error. This was supported by Papadopoulos and Giauque [48] who showed that Brackett's heat capacity measurements agree with unpublished data of Schutz.

Hepler and Olofsson [49] have critically reviewed the potentials for the mercurous sulfate–mercury reference electrode, and IUPAC [42] has accepted their standard electrode potential of 0.613 V. This value appears to be an average of the value of Covington *et al.* [31] and Gardner *et al.* [34] of 0.6125 and values of 0.6135 computed from the solubility product for Hg₂SO₄ of Brown and Laud [50] and 0.6136 from e.m.f. measurements of Sharma and Prasad [51]. Averaging values may not be the best approach, however, because of differences in K_2 values used to generate the E° values. The higher standard potential calculated from the solubility product of Brown and Laud is based on a K_2 value of 0.0120, which they used to calculate the solubility product for mercurous sulfate in sulfuric acid. Sharma and Prasad used a K_2 value of 0.011. These values are higher than that of 0.0102 recommended by Wirth [35] based on the works of Covington and Gardner. More recently, Mussini and coworkers have determined an E° value for the mercurous sulfate electrode of 0.612 57 V [52] and a K_2 value of 0.010 39 [53] based on e.m.f. measurements of Na_xHg_{1-x}|Na₂SO₄(aq., m)|Hg₂SO₄|Hg.

One approach which can be used to determine the temperature dependence of the electromotive force is the 'third-law method' in which the heat capacities of the cell reactants and products are measured independently and used to determine the temperature dependence. As previously noted, Gardner *et al.* [34] used this approach to determine the activity coefficients for sulfuric acid from 5 to 55 °C. Duisman and Giauque [45] used the third-law method to calculate the temperature dependence of the open circuit voltage of the lead–acid cell. Their temperature coefficients of the cell potential agree closely with the cell data of Beck *et al.* [27] and therefore appear to be accurate. Table 2 shows the temperature coefficients given by Duisman and Giauque for acid concentrations from 0.1 to 13.877 m and temperatures from 0 to 60 °C. Duisman and Giauque noted that the accuracy of these values does

TABLE 2
Temperature coefficients of the lead-acid cell

m	$E_{288.15} - E_r$ (mV) of the lead storage cell from the third law of thermodynamics													
	273.15	278.15	283.15	288.15	293.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15		
T (K)														
0.1	-6.102	-4.713	-3.410	-2.191	-1.055	0.975	1.871	2.689	3.431	4.098	4.962	5.213		
0.2	-3.872	-2.943	-2.092	-1.319	-0.622	0.548	1.024	1.428	1.762	2.026	2.223	2.353		
0.3	-2.414	-1.785	-1.231	-0.749	-0.339	0.270	0.472	0.607	0.676	0.681	0.621	0.498		
0.4	-1.317	-0.914	-0.581	-0.319	-0.126	0.059	0.053	-0.017	-0.151	-0.347	-0.605	-0.923		
0.5	-0.400	-0.193	-0.050	0.029	0.045	-0.106	-0.271	-0.495	-0.776	-1.115	-1.509	-1.958		
0.6	0.351	0.399	0.387	0.316	0.187	-0.243	-0.542	-0.894	-1.301	-1.760	-2.272	-2.834		
0.7	1.005	0.913	0.766	0.564	0.308	-0.360	-0.772	-1.233	-1.744	-2.304	-2.911	-3.566		
0.8	1.606	1.801	1.113	0.791	0.420	-0.468	-0.982	-1.543	-2.150	-2.801	-3.496	-4.235		
0.9	2.135	1.851	1.421	0.993	0.519	-0.563	-1.171	-1.821	-2.513	-3.248	-4.023	-4.839		
1.0	2.620	2.180	1.698	1.173	0.607	-0.647	-1.334	-2.059	-2.823	-3.624	-4.462	-5.337		
1.110	3.063	2.528	1.953	1.339	0.688	-0.725	-1.485	-2.281	-3.112	-3.977	-4.875	-5.807		
1.388	4.020	3.280	2.508	1.704	0.867	-0.898	-1.826	-2.784	-3.771	-4.787	-5.831	-6.903		
1.850	5.175	4.194	3.185	2.150	1.088	-1.113	-2.251	-3.414	-4.601	-5.812	-7.046	-8.303		
2.220	5.702	4.162	3.496	2.355	1.189	-1.213	-2.449	-3.709	-4.990	-6.294	-7.620	-8.967		
2.775	6.081	4.912	3.720	2.503	1.263	-1.286	-2.593	-3.923	-5.274	-6.647	-8.040	-9.454		
3.172	6.168	4.982	3.771	2.537	1.280	-1.302	-2.627	-3.973	-5.341	-6.729	-8.138	-9.568		
3.700	6.002	4.854	3.679	2.478	1.252	-1.276	-2.577	-3.901	-5.249	-6.620	-8.014	-9.431		
4.626	5.256	4.270	3.250	2.199	1.115	-1.146	-2.322	-3.527	-4.762	-6.026	-7.318	-8.638		
5.551	4.134	3.437	2.674	1.846	0.954	-1.016	-2.092	-3.228	-4.423	-5.675	-6.984	-8.349		
6.167	3.651	3.056	2.393	1.661	0.863	-0.928	-1.919	-2.972	-4.087	-5.262	-6.497	-7.790		

6.938	3.171	2.674	2.107	1.472	0.769	-0.834	-1.732	-2.693	-3.717	-4.801	-5.945	-7.149
7.929	2.760	2.340	1.854	1.301	0.682	-0.745	-1.553	-2.422	-3.350	-4.338	-5.384	-6.487
8.539	2.641	2.238	1.772	1.242	0.651	-0.711	-1.481	-2.308	-3.192	-4.131	-5.126	-6.175
9.291	2.602	2.192	1.725	1.204	0.628	-0.681	-1.413	-2.195	-3.028	-3.909	-4.838	-5.815
10.092	2.647	2.207	1.721	1.191	0.617	-0.659	-1.360	-2.102	-2.884	-3.706	-4.567	-5.466
11.101	2.725	2.249	1.737	1.192	0.612	-0.645	-1.322	-2.030	-2.769	-3.539	-4.399	-5.168
12.335	2.797	2.290	1.756	1.197	0.611	-0.636	-1.296	-1.981	-2.689	-3.421	-4.176	-4.953
13.877	2.843	2.313	1.764	1.195	0.607	-0.626	-1.269	-1.931	-2.611	-3.308	-4.022	-4.753

TABLE 3
The potentials of the lead dioxide, lead sulfate electrode (cell D)

Temp. (K)	0.1000 m	0.1996 m	0.2917 m	0.4717 m	1.129 m	2.217 m	3.900 m	4.973 m	6.095 m	7.199 m
	e.m.f. (V)									
278.16	1.57410	1.59097	1.60031	1.61237	1.63738	1.66364	1.69856	1.71984	1.74035	1.75965
283.16	1.57173	1.58893	1.59833	1.61065	1.63606	1.66259	1.69743	1.71864	1.73891	1.75820
293.16	1.56730	1.58480	1.59450	1.60720	1.63336	1.66045	1.69524	1.71603	1.73640	1.75560
308.16	1.56509	1.58284	1.59266	1.60550	1.63195	1.65943	1.69420	1.71491	1.73516	1.75425
308.16	1.56086	1.57887	1.58896	1.60232	1.62948	1.65720	1.69212	1.71260	1.73285	1.75187
318.16	1.55683	1.57510	1.58544	1.59924	1.62701	1.65518	1.69013	1.71056	1.73073	1.74964
328.16	1.55284	1.57146	1.58197	1.59617	1.62455	1.65320	1.68826	1.70878	1.72856	1.74740

TABLE 4
The potentials of the mercurous sulfate-mercury reference electrode

Temp. (K)	0.1003 m	0.1745 m	0.3877 m	0.5530 m	0.9776 m	1.872 m	3.911 m	5.767 m	7.972 m
	e.m.f. (V)								
278.16	0.73866	0.72547	0.70589	0.69703	0.68099	0.65837	0.61977	0.59538	0.55985
288.16	0.73820	0.72461	0.70458	0.69536	0.67912	0.65582	0.61725	0.58717	0.55731
298.16	0.73775	0.72386	0.70320	0.69368	0.67676	0.65345	0.61430	0.58474	0.55490
308.16	0.73729	0.72301	0.70180	0.69201	0.67453	0.65065	0.61155	0.58203	0.55266
318.16	0.73678	0.72209	0.70025	0.69007	0.67241	0.64776	0.60857	0.57920	0.55042
328.16	0.73629	0.72116	0.69850	0.68858	0.67028	0.64491	0.60633	0.57614	0.54842

not depend on the accuracy of the cell potentials at 25 °C because they are determined independently.

The dependence of the potential of the lead dioxide, lead sulfate electrode versus a hydrogen electrode in the same acid concentration (Cell I) was determined by Beck *et al.* [32] for temperatures from 0 to 55 °C and acid concentrations from 0.1 to 8 m. These values are shown in Table 3. The dependence of the potential of the mercurous sulfate–mercury reference electrode versus a hydrogen electrode in the same acid concentration (Cell II) was determined by Beck *et al.* [27] for acid concentrations from 0.1 to 7.199 m and temperatures from 5 to 55 °C. These values are shown in Table 4. Because the only values for the activity of water in sulfuric acid in this temperature range are those of Harned and Hamer, calculation of the potential of the positive electrode of the lead–acid battery versus a mercurous sulfate–mercury reference electrode (Cell V) using the Nernst equation may not be the best method. Accurate half-cell potentials may be obtained over this temperature range by subtracting the potential for Cell II from the potential for Cell I at the same acid concentration and temperature, using the data of Beck *et al.* [42].

5. Conclusions

Three sets of data provide a consistent and apparently reliable set of activity coefficients for sulfuric acid from 5 to 55 °C and 0.1 to 4 m (76 m at 25 °C). These are: Covington *et al.* [31], Gardner *et al.* [34], and Robinson and Stokes [26, 33], as recalculated here and by Covington *et al.* using a more accurate reference activity coefficient. From 0.001 to 0.02 m the values of Shrawder and Cowperthwaite [16], as recalculated by Lilley and Briggs [17] at 25 °C, are recommended. These data are shown in Table 1 and Appendix I.

The best values for the activities of water at 25 °C are those of Giauque *et al.* [28] from 1 to 1000 m and Robinson and Stokes [26] from 0.1 to 76 m. These data are shown in Table 1 and Appendix II. At other temperatures and concentrations, the water activities of Harned and Hamer are apparently the only ones published.

A standard potential for the lead–acid cell which is consistent with the most accurate activity coefficients is 2.048 V at 25 °C. The e.m.f.s of the lead–acid cell at 25 °C calculated using the Nernst equation, $E^\circ = 2.048$ V, and the water activities and revised activity coefficients from the vapor pressure measurements of Robinson and Stokes [26, 33] are given in Table 1 for H₂SO₄ molalities from 0.1 to 30. The calculated e.m.f.s agree well with those determined from cell measurements.

The equations of Pitzer *et al.* [36–38] can be used to calculate the activity and osmotic coefficients of sulfuric acid, and the activities of water as a function of temperature as well as acid concentrations from 0.1 to 6.0 m. Pitzer's equations can also be used to calculate directly the potentials

of Cells I, II, and III, i.e., the e.m.f. of the lead–acid cell and its half-cell potentials versus a mercurous sulfate–mercury reference electrode.

The dependence of the cell e.m.f. on temperature can also be determined by the third-law method using independently measured heat capacities. Duisman and Giauque [45] have determined the temperature dependence of the open-circuit voltage of the lead–acid cell using this method. Their values, shown in Table 2, appear to be accurate and are useful for calculating the e.m.f. from 0 to 60 °C at concentrations from 0.1 to 13.877 m. The dependence of the potentials of the lead dioxide, lead sulfate electrode, and the mercurous sulfate, mercury reference electrode on temperature, from the work of Beck *et al.* [27, 32] is shown in Tables 3 and 4 for acid concentrations of 0.1 to 8 m and temperatures from 0 to 55 °C. From these data the half-cell potentials of the lead dioxide and lead electrodes can be calculated.

Work is presently ongoing to evaluate the literature on the solubilities of lead sulfate in sulfuric acid. Preliminary results [54] indicate that Pitzer's equations can be extended to these systems and used to fit the data over a wide range of acid concentrations and temperatures. The effect of the solubility of lead sulfate on the electrode potentials discussed in this paper has been neglected except for molalities below 2×10^{-2} . The solubility of lead sulfate increases at both very low and very high concentrations of sulfuric acid. The use of the Pitzer equations to fit and evaluate the data for the solubility of lead sulfate in sulfuric acid will be shown in a future paper. This information can then be used to evaluate the effect of lead sulfate solubilities on the cell potentials over a wide range of acid concentrations and temperatures.

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List of symbols

α_x	Activity of the designated species 'x'
E°	Standard potential
F	Faraday constant, $9.648\,456 \times 10^4$ C eq ⁻¹
K_1	Equilibrium constant for the first dissociation of sulfuric acid
K_2	Equilibrium constant for the second dissociation of sulfuric acid
m	Molality, moles solute/kg solvent
$M_{\text{H}_2\text{O}}$	Molecular weight of H ₂ O
R	Gas constant, $8.314\,41$ J mol ⁻¹ T ⁻¹
T	Absolute temperature, 298.15 K
γ	Activity coefficient
γ_\pm	Mean ionic activity coefficient
ϕ	Osmotic coefficient
ν	Number of ions into which a single electrolyte dissociates

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Appendix 1

Activity coefficients of aqueous sulfuric acid

Molality	Gamma
0 °C	
1×10^{-3}	8.53×10^{-1}
2×10^{-3}	7.98×10^{-1}
5×10^{-3}	7.00×10^{-1}
1×10^{-2}	$6.09[6.16 \times 10^{-1}]$
2×10^{-2}	5.16×10^{-1}
12.5 °C	
1×10^{-3}	8.46×10^{-1}
2×10^{-3}	7.82×10^{-1}
5×10^{-3}	6.74×10^{-1}
1×10^{-2}	$5.74 \times 10^{-1}[5.75 \times 10^{-1}]$
2×10^{-2}	4.78×10^{-1}
25 °C	
1×10^{-3}	$8.37 \times 10^{-1}(7.96 \times 10^{-1})$
2×10^{-3}	$7.67 \times 10^{-1}(7.30 \times 10^{-1})$
5×10^{-3}	$6.46 \times 10^{-1}(6.14 \times 10^{-1})$
1×10^{-2}	$5.43 \times 10^{-1}(5.16 \times 10^{-1})[5.36 \times 10^{-1}]$
2×10^{-2}	$4.44 \times 10^{-1}(4.22 \times 10^{-1})$
37.5 °C	
1×10^{-3}	8.28×10^{-1}
2×10^{-3}	7.52×10^{-1}
5×10^{-3}	6.23×10^{-1}
1×10^{-2}	$5.15 \times 10^{-1}[4.94 \times 10^{-1}]$
2×10^{-2}	4.16×10^{-1}
50 °C	
1×10^{-3}	8.07×10^{-1}
2×10^{-3}	7.25×10^{-1}
5×10^{-3}	5.96×10^{-1}

1×10^{-2}	$4.85 \times 10^{-1} [4.45 \times 10^{-1}]$
2×10^{-2}	3.86×10^{-1}

Shrawder and Cowperthwaite, 1934 [16]; values in parentheses recalculated by Lilley and Briggs, 1975 [17]; values in brackets recalculated by Pitzer, 1976 [37]. BOTH SETS OF RECALCULATED VALUES ARE RECOMMENDED.

25 °C

1×10^{-1}	$2.655 \times 10^{-1} (2.45 \times 10^{-1})$
2×10^{-1}	$2.090 \times 10^{-1} (1.93 \times 10^{-1})$
3×10^{-1}	$1.826 \times 10^{-1} (1.69 \times 10^{-1})$
4×10^{-1}	1.666×10^{-1}
5×10^{-1}	$1.557 \times 10^{-1} (1.44 \times 10^{-1})$
6×10^{-1}	1.477×10^{-1}
7×10^{-1}	$1.417 \times 10^{-1} (1.31 \times 10^{-1})$
8×10^{-1}	1.374×10^{-1}
9×10^{-1}	1.342×10^{-1}
1.0	$1.316 \times 10^{-1} (1.22 \times 10^{-1})$
1.2	1.283×10^{-1}
1.4	1.266×10^{-1}
1.5	$1.263 \times 10^{-1} * (1.17 \times 10^{-1})$
1.6	1.260×10^{-1}
1.8	1.264×10^{-1}
2.0	$1.276 \times 10^{-1} (1.18 \times 10^{-1})$
2.5	$1.331 \times 10^{-1} (1.23 \times 10^{-1})$
3.0	$1.422 \times 10^{-1} (1.31 \times 10^{-1})$
3.5	$1.547 \times 10^{-1} (1.43 \times 10^{-1})$
4.0	$1.700 \times 10^{-1} (1.57 \times 10^{-1})$
4.5	$1.875 \times 10^{-1} (1.73 \times 10^{-1})$
5.0	$2.081 \times 10^{-1} (1.92 \times 10^{-1})$
5.5	2.312×10^{-1}
6.0	$2.567 \times 10^{-1} (2.37 \times 10^{-1})$
6.5	2.852×10^{-1}
7.0	$3.166 \times 10^{-1} (2.92 \times 10^{-1})$
7.5	3.50×10^{-1}
8.0	$3.86 \times 10^{-1} (3.56 \times 10^{-1})$
8.5	4.26×10^{-1}
9.0	4.67×10^{-1}
9.5	5.12×10^{-1}
1.00×10^1	5.59×10^{-1}
1.10×10^1	6.61×10^{-1}
1.20×10^1	7.70×10^{-1}
1.30×10^1	8.88×10^{-1}
1.40×10^1	1.017
1.50×10^1	1.154
1.60×10^1	1.300
1.70×10^1	1.450

1.80×10^1	1.608
1.90×10^1	1.771
2.00×10^1	1.940
2.10×10^1	2.114
2.30×10^1	2.300

Stokes, 1948 [33] and *Robinson and Stokes, 1959 [26]; values in parentheses recalculated by Covington *et al.*, 1965 [31]. RECALCULATED VALUES ARE RECOMMENDED.

2.40×10^1	2.666
2.60×10^1	3.040
2.80×10^1	3.423
3.00×10^1	3.792
3.20×10^1	4.152
3.40×10^1	4.493
3.60×10^1	4.828
3.80×10^1	5.145
4.00×10^1	5.406
4.20×10^1	5.656
4.40×10^1	5.891
4.60×10^1	6.097
4.80×10^1	6.278
5.00×10^1	6.443
5.20×10^1	6.586
5.40×10^1	6.700
5.60×10^1	6.817
5.80×10^1	6.906
6.00×10^1	6.982
6.20×10^1	7.045
6.40×10^1	7.091
6.60×10^1	7.125
6.80×10^1	7.153
7.00×10^1	7.171
7.20×10^1	7.181
7.40×10^1	7.184
7.60×10^1	7.182

Robinson and Stokes, 1959 [26].

25 °C

1×10^{-2}	5.16×10^{-1} *
2×10^{-2}	4.20×10^{-1} *

Cell I II

1×10^{-1}	2.46, 2.44×10^{-1}
2×10^{-1}	1.93, 1.92×10^{-1}
3×10^{-1}	1.70, 1.68×10^{-1}
4×10^{-1}	1.56, 1.53×10^{-1}

5×10^{-1}	1.46, 1.43×10^{-1}
7×10^{-1}	1.32, 1.30×10^{-1}
1.0	1.22, 1.21×10^{-1}
1.5	1.16, 1.16×10^{-1}
2.0	1.17, 1.18×10^{-1}
2.5	1.23, 1.24×10^{-1}
3.0	1.32, 1.32×10^{-1}
3.5	1.43, 1.43×10^{-1}
4.0	1.57, 1.57×10^{-1}
4.5	1.73, 1.72×10^{-1}
5.0	1.92, 1.90×10^{-1}
6.0	2.37, 2.34×10^{-1}
7.0	2.92, 2.88×10^{-1}
8.0	3.61, 3.56×10^{-1}

Covington *et al.*, 1965 [31]; *calculated from Covington's data by Lillie and Briggs [17]. THESE VALUES ARE RECOMMENDED.

0 °C	
1×10^{-1}	2.94×10^{-1}
2×10^{-1}	2.35×10^{-1}
5×10^{-1}	1.77×10^{-1}
1.0	1.51×10^{-1}
1.5	1.46×10^{-1}
2.0	1.50×10^{-1}
2.5	1.60×10^{-1}
3.0	1.75×10^{-1}
4.0	2.13×10^{-1}
5 °C	
1×10^{-1}	2.85×10^{-1}
2×10^{-1}	2.26×10^{-1}
5×10^{-1}	1.70×10^{-1}
1.0	1.45×10^{-1}
1.5	1.40×10^{-1}
2.0	1.44×10^{-1}
2.5	1.53×10^{-1}
3.0	1.67×10^{-1}
4.0	2.02×10^{-1}
15 °C	
1×10^{-1}	2.66×10^{-1}
2×10^{-1}	2.10×10^{-1}
5×10^{-1}	1.57×10^{-1}
1.0	1.33×10^{-1}
1.5	1.28×10^{-1}
2.0	1.31×10^{-1}
2.5	1.38×10^{-1}

3.0	1.49×10^{-1}
4.0	1.78×10^{-1}
25 °C	
1×10^{-1}	2.44×10^{-1}
2×10^{-1}	1.92×10^{-1}
5×10^{-1}	1.43×10^{-1}
1.0	1.21×10^{-1}
1.5	1.15×10^{-1}
2.0	1.17×10^{-1}
2.5	1.23×10^{-1}
3.0	1.32×10^{-1}
4.0	1.56×10^{-1}
35 °C	
1×10^{-1}	2.21×10^{-1}
2×10^{-1}	1.71×10^{-1}
5×10^{-1}	1.29×10^{-1}
1.0	1.09×10^{-1}
1.5	1.04×10^{-1}
2.0	1.05×10^{-1}
2.5	1.09×10^{-1}
3.0	1.16×10^{-1}
4.0	1.35×10^{-1}
45 °C	
1×10^{-1}	1.99×10^{-1}
2×10^{-1}	1.55×10^{-1}
5×10^{-1}	1.16×10^{-1}
1.0	9.7×10^{-2}
1.5	9.1×10^{-2}
2.0	9.3×10^{-2}
2.5	9.7×10^{-2}
3.0	1.02×10^{-1}
4.0	1.17×10^{-1}
55 °C	
1×10^{-1}	1.77×10^{-1}
2×10^{-1}	1.38×10^{-1}
5×10^{-1}	1.02×10^{-1}
1.0	8.6×10^{-2}
1.5	8.2×10^{-2}
2.0	8.1×10^{-2}
2.5	8.3×10^{-2}
3.0	8.7×10^{-2}
4.0	9.9×10^{-2}

Gardner *et al.*, 1969 [34]. THESE VALUES ARE RECOMMENDED.

Appendix 2

Activities of water in sulfuric acid

Molality	Activity
25 °C	
3.0	8.515×10^{-1}
3.5	8.166×10^{-1}
4.0	7.800×10^{-1}
4.5	7.422×10^{-1}
5.0	7.033×10^{-1}
5.5	6.644×10^{-1}
6.0	6.260×10^{-1}
6.5	5.880×10^{-1}
7.0	5.509×10^{-1}
7.5	5.153×10^{-1}
8.0	4.813×10^{-1}
8.5	4.488×10^{-1}
9.0	4.180×10^{-1}
9.5	3.887×10^{-1}
1.00×10^1	3.612×10^{-1}
1.05×10^1	3.355×10^{-1}
1.10×10^1	3.112×10^{-1}
1.15×10^1	2.889×10^{-1}

Stokes, 1947 [25]. THESE VALUES ARE RECOMMENDED.

25 °C	
1×10^{-1}	9.9633×10^{-1}
2×10^{-1}	9.9281×10^{-1}
3×10^{-1}	9.8923×10^{-1}
5×10^{-1}	9.8190×10^{-1}
7×10^{-1}	9.7427×10^{-1}
1.0	9.6176×10^{-1}
1.5	9.3872×10^{-1}
2.0	9.1261×10^{-1}
2.5	8.836×10^{-1}
3.0	8.516×10^{-1}
3.5	8.166×10^{-1}
4.0	7.799×10^{-1}
4.5	7.422×10^{-1}
5.0	7.032×10^{-1}
5.5	6.643×10^{-1}
6.0	6.259×10^{-1}

6.5	5.879×10^{-1}
7.0	5.509×10^{-1}
7.5	5.152×10^{-1}
8.0	4.814×10^{-1}
8.5	4.488×10^{-1}
9.0	4.180×10^{-1}
9.5	3.886×10^{-1}
1.00×10^1	3.612×10^{-1}
1.10×10^1	3.111×10^{-1}
1.20×10^1	2.681×10^{-1}
1.30×10^1	2.306×10^{-1}
1.40×10^1	1.980×10^{-1}
1.50×10^1	1.698×10^{-1}
1.60×10^1	1.456×10^{-1}
1.70×10^1	1.252×10^{-1}
1.80×10^1	1.076×10^{-1}
1.90×10^1	9.25×10^{-2}
2.00×10^1	7.96×10^{-2}
2.10×10^1	6.86×10^{-2}
2.20×10^1	5.89×10^{-2}
2.30×10^1	5.06×10^{-2}
2.40×10^1	4.41×10^{-2}
2.60×10^1	3.31×10^{-2}
2.80×10^1	2.50×10^{-2}
3.00×10^1	1.91×10^{-2}
3.20×10^1	1.422×10^{-2}
3.40×10^1	1.547×10^{-2}
3.60×10^1	9.00×10^{-3}
3.80×10^1	7.11×10^{-3}
4.00×10^1	5.75×10^{-3}
4.20×10^1	4.67×10^{-3}
4.40×10^1	3.81×10^{-3}
4.60×10^1	3.15×10^{-3}
4.80×10^1	2.62×10^{-3}
5.00×10^1	2.20×10^{-3}
5.20×10^1	1.855×10^{-3}
5.40×10^1	1.585×10^{-3}
5.60×10^1	1.355×10^{-3}
5.80×10^1	1.168×10^{-3}
6.00×10^1	1.010×10^{-3}
6.20×10^1	8.82×10^{-4}
6.40×10^1	7.74×10^{-4}
6.60×10^1	6.84×10^{-4}
6.80×10^1	6.06×10^{-4}
7.00×10^1	5.37×10^{-4}
7.20×10^1	4.80×10^{-4}

7.40×10^1	4.30×10^{-4}
7.60×10^1	3.87×10^{-4}

Robinson and Stokes, 1959 [26]. THESE VALUES ARE RECOMMENDED.

25 °C

1	9.622×10^{-1}
2	9.130×10^{-1}
3	8.514×10^{-1}
4	7.800×10^{-1}
5	7.035×10^{-1}
6	6.257×10^{-1}
7	5.503×10^{-1}
8	4.806×10^{-1}
9	4.175×10^{-1}
1.0×10^1	3.611×10^{-1}
1.1×10^1	3.113×10^{-1}
1.2×10^1	2.678×10^{-1}
1.3×10^1	2.303×10^{-1}
1.4×10^1	1.980×10^{-1}
1.5×10^1	1.701×10^{-1}
1.6×10^1	1.462×10^{-1}
1.7×10^1	1.255×10^{-1}
1.8×10^1	1.077×10^{-1}
1.9×10^1	9.233×10^{-2}
2.0×10^1	7.929×10^{-2}
2.5×10^1	3.799×10^{-2}
3.0×10^1	1.937×10^{-2}
3.5×10^1	1.042×10^{-2}
4.0×10^1	5.90×10^{-3}
4.5×10^1	3.53×10^{-3}
5.0×10^1	2.23×10^{-3}
6.0×10^1	1.05×10^{-3}
7.0×10^1	5.80×10^{-4}
8.0×10^1	3.61×10^{-4}
9.0×10^1	2.47×10^{-4}
1.00×10^2	1.79×10^{-4}
2.00×10^2	3.20×10^{-5}
3.00×10^2	1.38×10^{-5}
4.00×10^2	7.87×10^{-6}
5.00×10^2	5.20×10^{-6}
1.000×10^3	1.50×10^{-6}

Giauque *et al.*, 1960 [28]. THESE VALUES ARE RECOMMENDED.