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THERMODYNAMIC PROPERTIES OF DILUTE SULFURIC ACID AND
THE POTENTIAL OF THE LEAD SULFATE-LEAD ELECTRODE

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(ABSTRACT)

The 1934 data of Shrawder and Cowperthwaite for the cell $\text{Pt}, \text{H}_2 | \text{H}_2\text{SO}_4(\text{m}) | \text{PbSO}_4, \text{Pb}, \text{Hg}$, which have been generally ignored, are shown to yield valuable information about the properties of sulfuric acid in the range below 0.02M and to give probably the best available value for the potential of the lead-lead sulfate electrode.

In 1934 Shrawder and Cowperthwaite¹ published measurements of the potential of the cell $\text{Pt}, \text{H}_2 | \text{H}_2\text{SO}_4(\text{m}) | \text{PbSO}_4, \text{Pb}, \text{Hg}$ over the range 0.001 to 0.02 M and 0 to 50°C. These data seem ideally suited to the determination of the thermodynamic properties of sulfuric acid below 0.02 M since the HSO_4^- is almost all dissociated in the most dilute solutions whereas it is roughly half dissociated at higher concentration. Surprisingly, neither the original authors nor anyone else to my knowledge has ever published a straightforward analysis of these measurements without unnecessary involvement of other data. Shrawder and Cowperthwaite used, in their own interpretation, the dissociation constants of Hamer² for HSO_4^- which have since been shown to be inaccurate. Subsequently, this work seems to have been ignored in consideration of the activity of sulfuric acid until Lilley and Briggs³ showed that, in the range of overlap (0.01 to 0.02 M), the Shrawder and Cowperthwaite results were in excellent agreement with those of Covington, et al.⁴ However, Latimer⁵ listed Shrawder and Cowperthwaite's value for the electrode potential.

Thus, it seems desirable to treat the Shrawder and Cowperthwaite data with a reasonable Debye-Hückel function including the limiting law but, so far as possible, without other assumptions which would bias the resulting standard cell potential and the implied solute standard state.

While the dissociation constant for HSO_4^- will enter the calculation, its value may be interlocked with assumptions about the activity coefficients of ions and, therefore, not be unambiguous.

Calculations

In addition to the measured cell potentials, Shrawder and Cowperthwaite¹ report the following quantity (actually its negative since they wrote the cell in the opposite direction).

$$E^{0'} = E - (RT/2F) \ln(4m^2m_2) \quad (1a)$$

$$= E^0 - (3RT/2F) \ln \gamma_+ \quad (1b)$$

Here m is the gross molality of the acid and m_2 is the molality of sulfate near the lead sulfate electrode assuming complete dissociation of HSO_4^- but also recognizing the solubility of lead sulfate.

For activity coefficients in this dilute range our assumed expression is

$$\ln \gamma_i = -z_i^2 A_\phi [I^{1/2}/(1+bI^{1/2}) + (2/b) \ln(1+bI^{1/2})] \quad (2)$$

where z_i is the number of charges on the i -th ion and A the Debye-Hückel parameter. This expression was derived recently⁶ from the Debye-Hückel distribution and the "pressure" equation of modern statistical mechanics. Use of the original Debye-Hückel expression

$$\ln \gamma_i = -z_i^2 A_\gamma I^{1/2}/(1+\rho I^{1/2}) \quad (3)$$

would give substantially the same results. Here $A_\gamma = 3A_\phi$. The assumed distance of closest interionic approach leads formally to the same value for b or ρ , but it is well-known that this feature of the theory is oversimplified and that b (or ρ) is best treated as an empirical parameter with a value near unity.

The bisulfate dissociation is given by the expression

$$K_2 = \frac{(2m-m_3)(m-m_3)}{m_3} \frac{\gamma_H \gamma_{SO_4}}{\gamma_{HSO_4}} \quad (4)$$

where m_3 is the molality of HSO_4^- , $(2m-m_3)$ that of H^+ and $(m-m_3)$ that of $SO_4^{=}$. Then the stoichiometric activity coefficient $\gamma_\pm$ is

$$\gamma_\pm^3 = \frac{(2m-m_3)^2 (m-m_3)}{4m^3} \gamma_H^2 \gamma_{SO_4}$$

The effect of higher terms in the activity coefficient expressions would be small in this concentration range. While we^{6,7} have used $b = 1.2$ as a standard value in the expression in equation (2) when higher terms for short range interactions are included, we explore the possible effects of such interactions by variation in b .

An iterative procedure was followed with an initial value K_2 and of m_3 assumed. First m_3 is iteratively refined to fit equation (4) with activity coefficients determined by equation (2) and with $I = 3m - 2m_3$. Next equations (1b), (2), and (5) yield a value of E^0 . This process is repeated with adjusted values of K_2 until the minimum in standard deviation of E^0 is located.

It was found that excellent agreement could be obtained except for the most dilute solutions at the higher temperatures where there was a moderate but systematic deviation. This is not surprising since these are the conditions where solubility of lead sulfate is expected to have the greatest effect. Although a correction was made¹ for most obvious effect of this solubility, there are other effects which cannot readily be predicted. Hence it seemed best to ignore the values for 0.001 M at and above 25° and those for 0.002 M at 37.5 and 50°C.

The results for 25°C with a range of values of b are given in Table I. The fit is excellent with a standard deviation of only 0.05 mV. While the smallest σ was found for $b = 2.0$, the minimum is very broad and one cannot select a precise value for b on this basis. The absolute values for E^0 (which include the correction factor $1 \text{ Int } V = 1.00033 \text{ Abs } V$) are not independent of b , but the uncertainty is quite small. Likewise the effect of b on γ_+ is small at 25°C.

In contrast the variation in K_2 with b is substantial. There is an intrinsic redundancy between b and K_2 which cannot be resolved from these data, at least. Hence it is meaningless to compare K_2 values from different sources unless the assumed activity coefficient expressions are considered simultaneously.

Although the optimum b for 25° is greater than 1.2, that value, used elsewhere^{6,7} as a standard, is within the acceptable range and was used for treatment of the data at other temperatures.

The results are given in Table II. Activity coefficients at other molalities can be obtained, either from the parameters and equations (2), (4), and (5), or by correcting the originally published values¹ by the same ratio as for 0.01 M.

The values of K_2 in Table II have meaning only in relation to equation (2) and the value $b = 1.2$ used there. The effect of reasonable variation of b on E^0 and $\gamma_{\pm}$ is small at 25° as shown in Table I and is even less at lower temperatures (only 0.1 mV at 0°). At higher temperatures the uncertainties become considerably greater with an uncertainty of 1 mV or more for E^0 at 50°C.

The temperature coefficient of the K_2 values in Table II corresponds to a ΔH of dissociation of about -6 kcal/mole at 25°. This is somewhat larger the value -5.2 from both calorimetry⁸ and other sources.⁹ But this value of -6 kcal/mole is much more nearly correct than the value -2.2 implied by the dissociation constants of Hamer² which Shrawder and Cowperthwaite used in their own analysis of these data.

Discussion

The primary conclusion of this work is that the Shrawder and Cowperthwaite¹ results, which have been ignored in most studies of sulfuric acid, should be included in determining the properties in the dilute region. Except for the most dilute points at the higher temperatures, these data are quite consistent with generally established equations for activity coefficients and the dissociation of HSO_4^- ion.

The E^0 value at 25° from Table I may be taken as $-351.3 \pm .3$ mV. For comparison one may consider two values from combinations of other cells. Briggs and Lilley¹⁰ obtain $-352.6 \pm .4$ mV from determinations involving a membrane electrode for Ca^{++} in cells with CaCl_2 and the AgCl , Ag electrode and with CaSO_4 and the PbSO_4 , Pb , Hg electrode. Combination of the E^0 values for the AgX , Ag electrodes,⁷ the cells⁷ $\text{Hg}, \text{Zn}|\text{ZnX}_2(\text{m})|\text{AgX}, \text{Ag}$ (with $\text{X} = \text{Cl}$ and Br), and the cell¹¹ $\text{Hg}, \text{Zn}|\text{ZnSO}_4(\text{m})|\text{PbSO}_4, \text{Pb}, \text{Hg}$ yield values in the range -349.4 to -350.2 mV. In view of the possible accumulation of error in combinations of data from several cells, the result for the single cell discussed in this paper seems preferable at or below 25°C .

At higher temperatures, the interpretation of the results of Shrawder and Cowperthwaite becomes more ambiguous; hence indirect measurements of the PbSO_4 , Pb potential could yield a more accurate value and could then be used together with the present data to obtain a more accurate description of the properties of dilute sulfuric acid.

As noted above, the values of the dissociation constant K_2 for HSO_4^- are interlocked with assumptions about activity coefficients of the ions. Covington, et al,⁴ recognized this situation in their recent discussion. For 25° they recommend $0.0106 \pm .0009$ for K_2 although their own experimental results indicate a slightly higher range $0.0111 \pm .0006$. These authors used equation (3) with ρ values from 1.0 to 1.7 for activity coefficients of the ions. The results of Table I

correspond to $K_2 = 0.012_5 \pm .001_5$ with a wider range of values of b than was used for ρ . While our value of K_2 is higher, there is no conflict when uncertainties in interpretation are considered.

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TABLE I: Parameters of Activity Coefficient
Equations Fitted to Cell Potentials for 25°C

b	$-\ln K_2$	$\sigma(E)/\text{mV}$	$-E^0/\text{mV}$	$\gamma_{\pm}(m=0.01)$
0.8	4.23	0.06_6	350.97	0.538
1.0	4.27	$.05_3$	351.07	.537
1.2	4.30	$.04_5$	351.14	.536
1.5	4.35	$.03_5$	351.28	.534
2.0	4.41	$.03_4$	351.43	.532
3.0	4.50	$.05_2$	351.64	.529

TABLE II: Standard Potentials and Activity
Coefficients at Various Temperatures (with $b=1.2$)

$t, ^\circ\text{C}$	$-E^0/\text{mV}$	$\gamma_{\pm} (m=0.01)$	$-\ln K_2$
0.0	327.78	0.616	3.39
12.5	339.21	.575	3.88
25.0	351.14	.536	4.30
37.5	363.7	.494	4.69
50.0	377.5	.445	5.14

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