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Reviews

High Temperature Dissociation Constants of HS^- and the Standard Thermodynamic Values for S^{2-}

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The magnitude of the dissociation constant for $HS^- = S^{2-} + H^+$ at saturation vapor pressure, 25 °C, and infinite dilution is $\log K_{2a}^{\ominus} = -14.0 \pm 0.2$. The value of $\Delta G_{2a}^{\ominus} = (79.9 \pm 2.3)$ kJ·mol^{-1}, calculated from this $\log K_{2a}^{\ominus}$, was combined with the calorimetric enthalpy $\Delta H_{2a}^{\ominus} = (54.8 \pm 1.7)$ kJ·mol^{-1}, to obtain the entropy of dissociation, $\Delta S_{2a}^{\ominus} = (-84.2 \pm 30.0)$ J·K^{-1}·mol^{-1}. Consistent standard thermodynamic values for the aqueous species S^{2-} obtained from these data are as follows: $\Delta_f G° = (91.9 \pm 2.3)$ kJ·mol^{-1}, $\Delta_f H° = (38.7 \pm 1.8)$ kJ·mol^{-1}, and $S° = (-16.0 \pm 10.0)$ J·K^{-1}·mol^{-1}. The standard heat capacity of S^{2-}, $C_p° = (-284 \pm 60)$ J·K^{-1}·mol^{-1}, was calculated from a correlation between $C_p°$ and $S°$. The heat capacity of dissociation, $\Delta C_{p,2a}^{\ominus} = (-192 \pm 60)$ J·K^{-1}·mol^{-1}, was calculated from $C_p°$ for HS^- and this $C_p°$ for S^{2-}. The change in $R \ln K_{2a}$ with temperature was computed up to 300 °C and compared with experimental data from the literature. The standard potential for S(rhomb) + 2e → S^{2-} at 25 °C and infinite dilution is $E^{\ominus} = (-0.476 \pm 0.004)$ V. Published experimental data with the more negative $\log K_{m,2a} = -17$ were rejected because, while valid in, for example, (12 to 17) mol·L^{-1} NaOH solutions, they could not be calculated with confidence to the standard condition of infinite dilution.

Introduction

Dissolved H_2S gas dissociates in aqueous media to form HS^-, which can dissociate to S^{2-}. Values of the two dissociation constants up to high temperatures are needed: for sulfide ore stability studies at 25 °C in the form of potential−pH diagrams[1]; in the deposition of thin films of CdS for solar cells applications[2] prepared by reaction between thiourea, which undergoes hydrolysis to form undissociated H_2S(aq), and cadmium acetate at 85 °C; for the electrochemical production of hydrogen and sulfur[3] by oxidation of equimolar solutions of NaHS and NaOH at 80 °C; in the sol−gel synthesis of semiconducting germanium disulfide[4] prepared from the hydrolysis product of germanium ethoxide and H_2S(g) at a temperature of 20 °C; to model the geochemistry of sulfide hydrothermal systems[5] up to 350 °C; for polysulfide electrolyte batteries;[6] and in hydrometallurgy for the treatment of sulfide ores.[7] However, while there are consistent experimental data for the first constant,[8] values of the second, eq 1, appear to vary over 5 orders of magnitude at 25 °C, are widely scattered, and have been the subject of a number of publications[9] from the year 1971 to 1998.

The threefold purpose of this work is to tabulate consistent standard thermodynamic values for the sulfide ion, then to use these values in calculating equilibrium constants up to 300 °C for eq 1, and to resolve the question of the apparent wide discrepancy in values for the second dissociation constant of H_2S(aq). The standard thermodynamic values for S^{2-} were to be obtained by computer fitting a selected set of consistent high temperature equilibrium constants for eq 1 to the mathematical model derived by Clarke and Glew.[10] A consistent set was to be obtained from published experimental studies. The research literature was examined for $K_{m,2a}$ values from the year 1900 to 1999.

Kury et al.[11] measured the calorimetric enthalpy of neutralization on solutions of H_2S(aq)

$$HS^- = S^{2-} + H^+ \qquad (1)$$

reacted with various mole ratios of NaOH/H_2S at (25.0 ± 0.5) °C. These data were plotted to zero ionic strength to obtain a standard enthalpy, $\Delta H_{2b}^{\ominus} = (49.7 \pm 3.4)$ kJ·mol^{-1}. Kury et al.[11] then calculated $\log K_{2a}^{\ominus} = -12.9 \pm 0.1$ from the value of K_{2a} at 20 °C.[12] Kury et al.[11] calculated $\Delta G_{2a}^{\ominus}$ and $\Delta S_{2a}^{\ominus}$ for the neutralization reaction, followed by computation of standard values for $\Delta_f G°$, $\Delta_f H°$, and $S°$ for S^{2-} with $\Delta_f G°$, $\Delta_f H°$, and $S°$ values for the species H_2O(l), OH^-, and H_2S(aq). Stephens and Cobble[13] made detailed measurements of the calorimetric enthalpy of solution of KHS in KOH solutions at 25 °C and 90 °C. Because the enthalpy of neutralization is small, in some experiments excess KOH was added to the final desired ionic strength to force the equilibrium for the reaction KHS(aq) + KOH(aq) = K_2S(aq) + H_2O(l) further to the right, thereby forming additional sulfide ion, if any, to ensure an accurate measurement of the enthalpy of neutralization, $\Delta H_{2b}^{\ominus}$. Their $\Delta H_{2a}^{\ominus} = (54.8 \pm 1.7)$ kJ·mol^{-1} was calculated for eq 1 with $\Delta H_w^{\ominus} = 55.535$ kJ·mol^{-1} for water, and their $\Delta H_{2b}^{\ominus} = (-945.6 \pm 1615)$ J·mol^{-1} for the reaction between KHS(aq) and KOH(aq). To obtain a value of $\log K_{2a}^{\ominus}$ for eq 1, Stephens and Cobble[13] compiled a database consisting of

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nine values of log $K_{m,2a}$ at ionic strengths from zero to 0.5 molality, in the temperature range (0 to 90) °C. However, this set of nine values appears inconsistent because not all were calculated to infinite dilution. For 0 °C, p$K_2 = 14.7$ is at an ionic strength[23] of 0.05 mol·L^{-1}. At 20 °C, the experimental apparent equilibrium constant p$K_{2a} = 14.15 \pm 0.05$[14] was measured in 1 mol·L^{-1} KCl solutions and notcalculated to infinite dilution. The value p$K_{2a} = 14.0 \pm 0.1$[22] was obtained at 22 °C in 1.0 mol·kg^{-1} NaOH solutions; at 50 °C, p$K_{2a} = 12.9 \pm 0.2$[22] was measured in 0.5 mol·kg^{-1} NaOH solutions; at 90 °C, p$K_{2a} = 12.0 \pm 0.2$[22] was measured in 0.1 mol·kg^{-1} NaOH. Because their database is inconsistent, their calculation of $\Delta S_{2a}^{\ominus}$ for eq 1, as well as their calculated standard thermodynamic values for the aqueous species S^{2-}, $\Delta_f G°$ and $S°$, can have unknown uncertainties, related to the added uncertainty in their selected log $K_{2a}^{\ominus} = -13.8$. However, their value for the standard enthalpy of dissociation, $\Delta H_{2a} = (54.8 \pm 1.7)$ kJ·mol^{-1} is independent of their database with the inconsistent pK_{2a} values and is used in this work. For the species S^{2-}, they calculated $\Delta_f G° = (90.8 \pm 0.8)$ kJ·mol^{-1}, $\Delta_f H° = (37.2 \pm 1.7)$ kJ·mol^{-1}, and $S° = (-17.1 \pm 8.4)$ J·K^{-1}·mol^{-1}. A standard value for the heat capacity $C_p° = (-439 \pm 38)$ J·K^{-1}·mol^{-1} relative to $C_p° = -130$ J·K^{-1}·mol^{-1} for H^+ was estimated from the difference in ΔH_{2a} at 25 °C and 90 °C. Giggenbach[15] reported a room temperature (24 °C) log $K_{m,2a} = -17.1 \pm 0.2$ for highly alkaline solutions such as 14 mol·L^{-1} NaOH. Rao and Hepler[7] examined extensive data for $K_{m,2a}$ from about 1905 up to 1971 and recommended as the standard values log $K_{2a}^{\ominus} = -13.78$ and $\Delta H_{2a}^{\ominus} = 54.8$ kJ·mol^{-1}. Rao and Hepler[7] further concluded that a $K_{2a}^{\ominus}$ substantially more negative than log $K_{2a}^{\ominus} = -13$ such as[15] log $K_{m,2a} = -17$ is inconsistent with the concentration dependent calorimetric measured enthalpies of neutralization. Over the next two and a half decades, other work included p$K_{m,2a} = 17.1 \pm 0.3$ in concentrated solutions[16] and log $K_{m,2a} = -17 \pm 1$ in 16.9 mol·L^{-1} NaOH.[17] Recently, Eckert[9] measured the pS^{2-} of hydrogen sulfide solutions from pH 6 to pH 11 with a pH_2S (glass/Ag°,Ag_2S) electrode and reported p$K_{m,2a}^{\ominus} = 13.86 \pm 0.05$ in 0.1 mol·L^{-1} KNO_3 solutions and in solutions with KNO_3 concentrations in the range $0.001 < I/\text{mol·L}^{-1} < 0.002$. Calibration of the p$S^{2-}$ cell was based on p$K_{sp} = 50.1$, the literature value for Ag_2S.

Mathematical Model

The dissociation constants $K_{m,2a}$ for eq 1 are defined by eq 2.

$$K_{m,2a} = m[S^{2-}]m[H^+]/m[HS^-]m° \tag{2}$$

In eq 2, the equilibrium quotient is divided by $m° = 1$ mol·kg^{-1}, the standard molality, to make $K_{m,2a}$ dimensionless. The standard state at each temperature for an ionized electrolyte such as HS^- in aqueous solution is the hypothetical state of the pure ions dissolved in pure water to give an ideal solution at unit mean moles per kilogram, at saturation vapor pressure.[8] Equation 1 specifies that when HS^- dissociates spontaneously in aqueous solutions, the result is equal concentrations of S^{2-} and H^+. The model assumes the absence of side reactions such as oxidation or polysulfide formation. An increase in pH caused by the addition of stoichiometric or an excess of hydroxide such as NaOH to solutions of H_2S(aq) or HS^- is typically used to measure the magnitude of $K_{m,2a}$ after correcting for the dissociation constant of water, K_w, but this is a neutralization reaction, $HS^- + OH^- = S^{2-} + H_2O(l)$, rather than the model, eq 1.

For this work, the mathematical model of Clarke and Glew,[10] relating apparent equilibrium constants such as $K_{m,2a}$ to thermodynamic data, is used in the form[18] of eq 3,

$$R \ln K_{2a} = A + B\,\text{K}/T + C \ln T/\text{K} + DT/\text{K} \tag{3}$$

$$A = \Delta S_{2a}^{\ominus} - C_0 - \ln \theta(C_0 - \theta C_1)$$

$$B = -\Delta H_{2a}^{\ominus} + \theta C_0 - {}^1\!/_2\theta^2 C_1$$

$$C = C_0 - \theta C_1$$

$$D = {}^1\!/_2 C_1$$

$$\text{and} \quad \theta = 298.15; \quad C_0 = \Delta C_{p,2a}^{\ominus}; \quad C_1 = (\text{d}\Delta C_{p,2a}/\text{d}T)^{\ominus}$$

where the molar gas constant[19] $R = 8.314\,510$ J·K^{-1}·mol^{-1}. In eq 3, K_{2a} denotes the dimensionless temperature dependent dissociation constant for eq 2, at infinite dilution. The superscript $\ominus$ identifies the standard thermodynamic values at 25 °C, saturation vapor pressure, and infinite dilution.

Additional terms with higher powers of T/K and higher derivatives of $\Delta C_{p,2a}^{\ominus}$ were not justified for this work because of the scarcity of experimental data. Thermodynamic quantities at saturation vapor pressure, 25 °C, and $I = 0$ mol·kg^{-1} are as follows:[18] $\Delta S_{2a}^{\ominus}$, entropy of dissociation; $\Delta H_{2a}^{\ominus}$, enthalpy of dissociation; $\Delta C_{p,2a}^{\ominus}$, heat capacity change for eq 1; $(\text{d}\Delta C_{p,2a}/\text{d}T)^{\ominus}$, the first derivative of the heat capacity change in eq 1.

Equation 3 predicts that a plot of $R \ln K_{m,2a}$ versus $(\text{K}/T)^{-1}$ will be a straight line with intercept $\Delta S_{2a}^{\ominus}$ at $(\text{K}/T)^{-1} = 0$ and with a slope $\Delta H_{2a}^{\ominus}$ only if the heat capacity change and its derivative are zero. Otherwise, the shape of the plot is determined by the magnitude of the thermodynamics of dissociation as defined by the coefficients A, B, C, and D. An advantage of eq 3 is that the variation in heat capacity with temperature is taken into account by inclusion of the heat capacity derivative.

Tabulation of Experimental Data for Fitting to Eq 3

The experimental data in Table 1 selected for fitting to eq 3 are at temperatures ranging from (0 to 90) °C, with electrolyte concentrations up to 2.46 mol·kg^{-1}. Maronny[20] calculated four experimental values of p$K_{m,2a}$ at 0 °C and four at 25 °C in sulfide solutions to zero ionic strength with the Debye−Hückel equation and obtained p$K_{2a} = 14.62$ at 0 °C and p$K_{2a}^{\ominus} = 13.78$ at 25 °C. These values were used here as published. Ellis and Golding[21] measured values of $K_{m,2a}$ in (0.25 to 2.46) mol·kg^{-1} solutions of NaOH, (0.25 to 5.00) mol·kg^{-1} KOH, and 1.00 mol·kg^{-1} LiOH, with total sulfide concentrations of $(0.5 \text{ to } 7) \times 10^{-4}$ mol·kg^{-1}, at 20 °C. These solutions were prepared in oxygen free water and transferred under a nitrogen atmosphere, to prevent oxidation of S^{2-}. The equilibrium concentrations of HS^- were measured at 20 °C with a spectrophotometer at 230 nm, where the species HS^- has an intense absorption band. Total aqueous sulfur, $(0.01 \text{ to } 3) \times 10^{-4}$ mol·L^{-1}, was determined by iodometric titration. The value of pK_{2a} was obtained from the slope of plots of [HS^-] versus total sulfide. Although each value of log $K_{m,2a}$ was obtained from about six replicate determinations, only one value is reported in the publication, and these do not have uncertainties. A log $K_{2a} = -14.00$ at 20 °C was obtained by extrapolation of pK_{2a} values versus hydroxide concentration from 0.25 mol·kg^{-1} to infinite dilution. However, the data

Table 1. Experimental Data Selected for $HS^- = S^{2-} + H^+$, Identified by Authors, and Referenced in the Literature Cited[a]

t/°C	I/mol·kg^{-1}	log $K_{m,2a}$	ref
0	0 (sulfide)	−14.62 ± 0.02[b]	20
0	0.05	−14.70 ± 0.05[b]	23
20	0.25 (NaOH)	−13.96 ± 0.08[b]	21
20	0.50 (NaOH)	−13.97 ± 0.08[b]	21
20	1.00 (NaOH)	−13.96 ± 0.08[b]	21
20	2.46 (NaOH)	−14.00 ± 0.08[b]	21
20	0.25 (KOH)	−13.91 ± 0.08[b]	21
20	0.50 (KOH)	−13.81 ± 0.08[b]	21
20	1.00 (KOH)	−13.83 ± 0.08[b]	21
20	2.00 (KOH)	−14.01 ± 0.08[b]	21
20	1 mol·L^{-1} (KCl)	−14.15 ± 0.05	14
22	0.1 (NaOH)	−13.6 ± 0.2	22
22	0.5 (NaOH)	−13.9 ± 0.2	22
22	1.0 (NaOH)	−14.0 ± 0.1	22
25	0 (sulfide)	−13.78 ± 0.02[b]	20
25	0.1 mol·L^{-1} (KNO_3)	−13.86 ± 0.05	9
25	0	−13.8 ± 0.3[c]	13
50	0.5 (NaOH)	−12.9 ± 0.2	22
90	0.1 (NaOH)	−12.0 ± 0.2	22
90	0.5 (NaOH)	−11.9 ± 0.2	22
90	1.0 (NaOH)	−12.2 ± 0.1	22

[a] Symbols: $K_{m,2a}$, temperature and concentration dependent equilibrium constant for eq 2. The uncertainties (±) are those assigned by the authors of each publication unless noted otherwise. [b] Estimated uncertainty, this work. [c] Calculated with the standard values in their Table 6.

for hydroxide concentrations < 0.25 mol·kg^{-1} are not included in their publication.

Ellis and Milestone[22] applied the spectrophotometric method to the determination of $K_{m,2a}$ at temperatures of 22 °C, 50 °C, and 90 °C. The UV−vis absorption peak for the HS^- species is shifted from 230 nm at 22 °C to 236 nm at 90 °C. They measured p$K_{m,2a}$ values in 0.1, 0.5, and 1.0 mol·kg^{-1} NaOH solutions but did not calculate these to infinite dilution. Widmer and Schwarzenbach[14] measured p$K_{m,2a}$ = 14.15 ± 0.05 in 1 mol·L^{-1} KCl solutions. Eckert[9] investigated a pH_2S electrode for the measurement of both p$K_{m,1a}$ and p$K_{m,2a}$. The electrochemical cell was calibrated at pH 5.0 in 0.1 mol·L^{-1} KNO_3. The pS^{2-} cell was calibrated versus the Ag(cr)/AgCl(cr) cell at two different silver activities. Weighed quantities of $Na_2S·9H_2O$(cr) under an inert nitrogen atmosphere were added to the cell, and the pH was lowered by the addition of a 1 mol·L^{-1} HCl solution. Three series of experimental data are published: 24 values obtained in the range $(0.001 < I < 0.002)$ mol·L^{-1}, seven at $I = 0.1$ mol·L^{-1} KNO_3 with total sulfide = (5.45×10^{-4}) mol·L^{-1}, and eight at $I = 0.1$ mol·L^{-1} KNO_3 with total sulfide = (1.70×10^{-4}) mol·L^{-1}. At 25 °C, log $K_{m,2a}$ = −13.86 ± 0.05 in 0.1 mol·L^{-1} KNO_3 solutions. Stephens and Cobble[13] used log $K_{2a}^{\ominus}$ = −13.78 on the basis of their nine tabulated values of log $K_{m,2a}$ over the temperature range (0 to 90) °C, and Jellinek and Czerwinski[23] obtained log $K_{m,2a}$ = −14.7 in I = 0.05 mol·L^{-1} solutions at 0 °C. These three values[9,13,23] are included in Table 1.

Kury et al.[11] estimated log $K_{2a}^{\ominus}$ = −12.9 from the value of Kubli[12] at 20 °C, calculated to 25 °C. This value is almost one unit of log K_{2a} more positive than the other values in Table 1 and was not used in this work. The $K_{m,2a}$ data at high concentrations of NaOH and KOH[15,16,17] were excluded because these data cannot be calculated with confidence to infinite dilution. The extensive values from (0 to 250) °C calculated by Dickson[24] from the solubility of cinnabar (HgS) were measured at a pressure of 1 MPa, rather than saturation vapor pressure, and were not included in Table 1.

Procedure for Obtaining K_{2a} Values at Infinite Dilution

The data in Table 1 have been organized according to increasing temperature and increasing electrolyte concentration, I, at each temperature. These data and uncertainties in the log $K_{m,2a}$ values were obtained from the publications, unless noted otherwise. Eckert's[9] log $K_{m,2a}$ = −13.86 ± 0.05 was calculated to the infinite dilution value log $K_{2a}^{\ominus}$ = −14.28 ± 0.05 with the Davies equation.[25] Widmer and Schwarzenbach[14] published log $K_{m,2a}$ = −14.15 ± 0.05 in 1 mol·L^{-1} KCl solutions at 20 °C. A calculation for converting from moles per liter gave 1 mol·kg^{-1}. This value was combined with those of Ellis and Golding.[21] The data at each temperature were fitted to eq 4 with the LINEST array function in Microsoft Excel.[26] The highest concentration was restricted to [OH^-] < 3.0 mol·kg^{-1}. The LINEST function applies a statistical analysis of data that are fitted to a straight line. The data are inputted to two selected rows of a spreadsheet, and then the command =LINEST(data range, TRUE,TRUE) is typed into a specified cell system. After LINEST is activated via the computer keyboard, the statistical analysis is displayed in designated cells in a format that prints the value of the slope and its standard error, the value of the intercept and its standard error, the standard error of the left-hand side of eq 4, and how closely the input data approximate a straight line, according to the coefficient of determination, R^2. The closer R^2 is to the ideal value, 1.00, obtained when all data fall exactly on a straight line, the better is the fitting of the data to a straight line. Consequently, the uncertainty in the extrapolated value, log K_{2a}, should be at its minimum.

The spectrophotometric data at 20 °C from Ellis and Golding[21] for (0.25 to 2.46) mol·kg^{-1} NaOH and for (0.25 to 2.00) mol·kg^{-1} KOH were fitted to the extended Debye−Hückel equation,[25] eq 4.

$$\log K_{m,2a} - A_\gamma \Delta z^2 (I^{1/2}/(1 + I^{1/2})) = \log K_{2a} + bI \qquad (4)$$

In eq 4, I is the ionic strength at temperature t/°C; A_γ is the temperature dependent Debye−Hückel parameter for activity coefficients[27,28] tabulated in Table 2; b is a temperature dependent constant; and $\Delta z^2 = 4$ is the sum of the squares of the charges of the products minus those of the reactants in eq 1.

The values of R^2 for the three sets of data at 20 °C, 22 °C, and 90 °C were 0.788, 0.914, and 0.995, respectively. These were interpreted as reasonable fittings to a straight line, reflecting in part that the data at 20 °C were from more than one laboratory and could be expected to show more scattering than the data at 22 °C and 90 °C obtained by one laboratory. There is only one log $K_{m,2a}$ at 50 °C. In this case, the magnitude of the parameter $b = -0.96$ kg·mol^{-1} was estimated by linear interpolation of $b = -1.00$ kg·mol^{-1} at 22 °C and $b = -0.90$ kg·mol^{-1} at 90 °C. The interpolated $b = -0.96$ kg·mol^{-1} is also consistent with the other two values measured by Ellis and Milestone.[22] This value of b was inserted into eq 4, and log K_{2a} = −13.2 was calculated at 50 °C.

Equation 4 predicts that a plot of the left-hand side versus ionic strength, I, is a straight line with intercept at $I = 0$ of log K_{2a} and slope b, for each temperature. Figure 1 is a plot of eq 4 for values of the function log $K_{m,2a} - A_\gamma \Delta z^2 (I^{1/2}/(1 + I^{1/2}))$ versus the ionic strength, I, at 20 °C,

Table 2. Values of the Debye–Hückel Parameter for Activity Coefficients, A_γ, at Saturation Vapor Pressures, for the Temperatures Shown,[27,28] Used in Eq 4[a]

t/°C	A_γ/(kg·mol^{-1})$^{1/2}$	log K_{2a}	b/kg·mol^{-1}	measure of closeness of fitting to a straight line, R^2
0	0.491	−14.62		
		−15.06		
20	0.505	−14.61	−0.29	0.788
		standard error: 0.07	standard error: 0.06	
22	0.507[b]	−14.08	−1.00	0.914
		standard error: 0.19	standard error: 0.31	
25	0.509	−14.28, −13.78, −13.8		
50	0.534	−13.2[c]	−0.96[c]	
90	0.585	−12.45	−0.90	0.995
		standard error: 0.04	standard error: 0.06	

[a] For eq 1, the parameter $\Delta z^2 = 4$. Fitted parameters at infinite dilution that were obtained at each temperature by linear regression of data in Table 1, with eq 4, using the Microsoft Excel Linest procedure,[26] are tabulated together with the standard errors for log K_{2a} and the parameter b. [b] Interpolated from the values of A_γ at 20 °C and 25 °C. [c] Interpolated from the two values of the parameter b, at 22 °C and 90 °C.

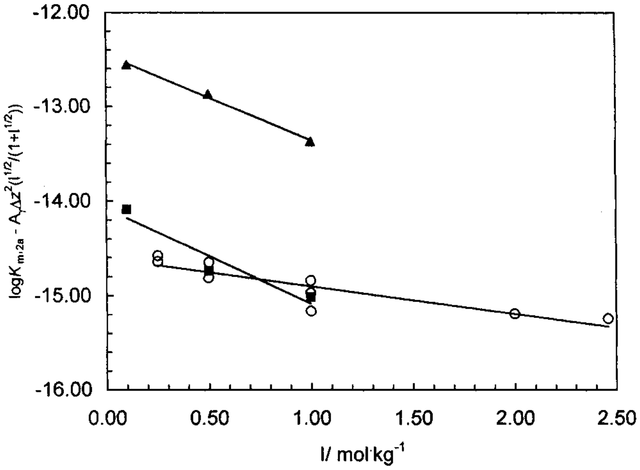

Figure 1. Linear change in log $K_{m,2a} - A_\gamma\Delta z^2(I^{1/2}/(1 + I^{1/2}))$ as a function of ionic strength, eq 4. The symbols for data obtained from Table 1: (○) 20 °C, Ellis and Golding,[21] Widmer and Schwarzenbach;[14] (■) 22 °C, Ellis and Milestone;[22] (▲) 90 °C, Ellis and Milestone.[22]

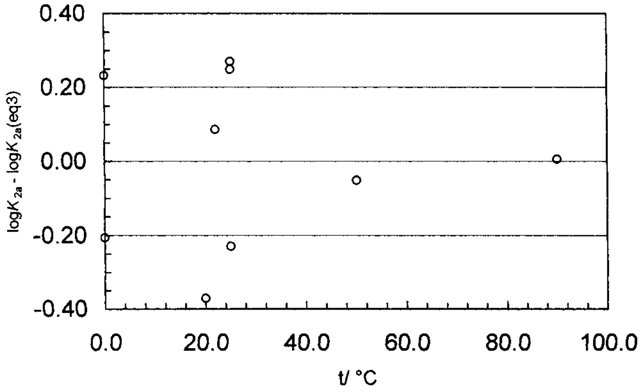

Figure 2. Deviation plot of the arithmetic difference, (log K_{2a} − log K_{2a}(eq 3)), as a function of temperature. The values of log K_{2a} are the nine experimental measurements of log K_{2a} calculated at infinite dilution, in Table 2. The log K_{2a}(eq 3) data are values from the computer fitting of log K_{2a} to eq 3.

22 °C, and 90 °C. Linear extrapolation of each plot results in the value of log K_{2a}, the dissociation constant at infinite dilution, at each temperature. The third column in Table 2 displays the resulting nine values of log K_{2a} from (0 to 90) °C at infinite dilution for inputting to eq 3, in the form of the Qbasic program, CGCALC.[29]

The nine selected equilibrium constants in Table 2 were fitted to eq 3 with CGCALC, a modification of SOLY1B[30] that runs on Qbasic. This program uses a least-squares method for obtaining the best fitting of the data to eq 3. The program then prints out the inputted data; the magnitudes of the four coefficients, A, B, C, and D; the estimated standard deviation for each coefficient; the input value of K_{2a} at each temperature compared with the values of K_{2a} computed from eq 3; and the standard values of $\Delta H_{2a}^{\ominus}$, $\Delta S_{2a}^{\ominus}$, $\Delta C_{p,2a}^{\ominus}$, and $d(\Delta C_{p,2a}/dT)^{\ominus}$ computed from eq 3. However, the inputted values of K_{2a} must be consistent, or else these four thermodynamic quantities will not be the standard values. In that case, the four coefficients A, B, C, and D have no thermodynamic significance and eq 3 is only applicable over the temperature range corresponding to the inputted data. The ideal data for CGCALC consist of equilibrium constants at uniform conditions of ionic strength that fall exactly on the curve described by eq 3. Less ideal data are acceptable, provided the derivative of the heat capacity is $< \pm 3$ J·K^{-2}·mol^{-1}.

The values of the coefficients for eq 1 are as follows: $A = (-92\,568.78 \pm 5.65)$ J·K^{-1}·mol^{-1}; $B = (2\,437\,515.3 \pm 1646.3)$ J·mol^{-1}; $C = (16\,121.92 \pm 0.99)$ J·K^{-1}·mol^{-1}; $D = (-25.93 \pm 0.02)$ J·K^{-2}·mol^{-1}. However, the heat capacity derivative is $(d\Delta C_{p,2a}/dT)^{\ominus} = -52$ J·K^{-2}·mol^{-1}, so that eq 3 is valid only from (0 to 90) °C. Figure 2 is a plot of the arithmetic difference between the nine selected K_{2a} values and the K_{2a}(calc) values obtained from the least-squares fitting at each temperature. The nine differences in value are within ±0.40 units of log K_{2a}. The plot in Figure 2 is interpreted as demonstrating the absence of any systematic trend as a function of temperature, that the errors are random, and that the data are a good fit to eq 3.

Thermodynamics of Dissociation of HS−

There are not sufficiently consistent K_{2a} measurements from (90 up to 300) °C to compute the standard enthalpy, entropy, heat capacity of dissociation, and derivative of the heat capacity with CGCALC. Instead, the average of log $K_{2a}^{\ominus} = -14.28$ and of log $K_{2a}^{\ominus} = -13.78$ from the data in Table 2, log $K_{2a}^{\ominus} = -14.0 \pm 0.2$, was taken as the value for eq 2. The enthalpy of dissociation[13] $\Delta H_{2a}^{\ominus} = (54.8 \pm 1.7)$ kJ·mol^{-1} was taken as the enthalpy of dissociation for eq 1. The Gibbs energy of dissociation $\Delta G_{2a}^{\ominus} = (79.9 \pm 2.3)$ kJ·mol^{-1} was calculated from $\Delta G_{2a}^{\ominus} = -RT \ln K_{2a}^{\ominus}$, and the entropy of dissociation, $\Delta S_{2a}^{\ominus} = (-84.2 \pm 30.0)$ J·K^{-1}·mol^{-1} was calculated from $\Delta G_{2a}^{\ominus} = \Delta H_{2a}^{\ominus} - 298.15\Delta S_{2a}^{\ominus}$. The standard entropy value for S^{2-}, $S° = (-16.0 \pm 10.0)$ J·K^{-1}·mol^{-1}, was obtained from this $\Delta S_{2a}^{\ominus}$ and the standard entropy[31] for HS$^-$, $S° = (68.2 \pm 0.2)$ J·K^{-1}·mol^{-1}, in Table 3. The uncertainty for the entropy values is estimated. The other estimated uncertainties were

Table 3. Standard Thermodynamic Values for Selected Sulfur and Oxygen Species, at Saturation Vapor Pressure, 25 °C, and Infinite Dilution[a]

formula	$\Delta_f G°$/kJ·mol^{-1}	$\Delta_f H°$/kJ·mol^{-1}	$S°$/J·K^{-1}·mol^{-1}	$C_p°$/J·K^{-1}·mol^{-1}
S(rhombic)	0[b]	0[b]	32.054 ± 0.050[b]	22.686 ± 0.050[b]
S^{2-}	91.9 ± 2.3[c]	38.7 ± 1.8[c]	−16.0 ± 10.0[c]	−284 ± 60[c]
H_2(g)	0[b]	0[b]	130.680 ± 0.005[b]	28.836 ± 0.002[b]
HS^-	11.98 ± 0.50[d]	−16.10 ± 0.50[d]	68.2 ± 0.2[d]	−92 ± 1[d]
OH^-	−157.24 ± 0.05[e]	−230.015 ± 0.040[e]	−10.71 ± 0.20[e]	−140.5 ± 4.0[e]
H_2O(l)	−237.141 ± 0.040[b]	−285.830 ± 0.040[b]	69.95 ± 0.03[b]	75.30[b]

[a] Symbols of standard thermodynamic values: Gibbs energy, $\Delta_f G°$; enthalpy, $\Delta_f H°$; entropy, $S°$; heat capacity, $C_p°$. The formula H_2O(l) identifies the liquid form of water. The standard state for S(rhombic) is this crystalline form under the standard-state pressure; the standard state for liquid water is that of the pure liquid under the standard-state pressure.[8] [b] Goldberg and Parker.[33] [c] This work. [d] Barbero et al.[31] [e] Phillips et al.[25]

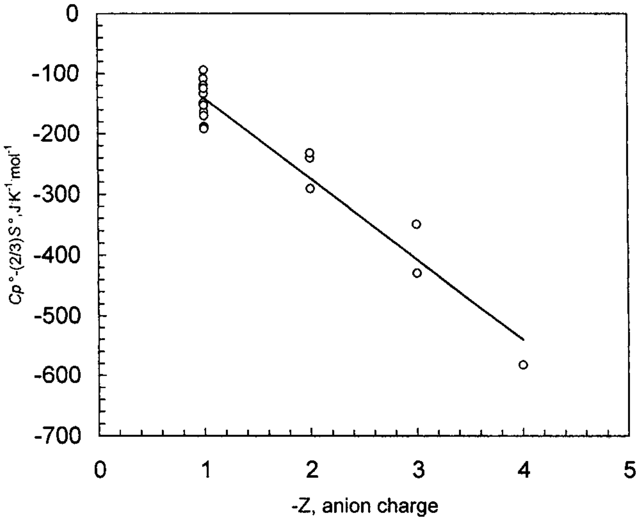

Figure 3. Plot of linear correlation between ($C_p° - {}^2/_3 S°$) and anion charge, $-z$, according to eq 5. The coefficient of determination, $R^2 = 0.929$, indicates a high degree of linearity of the fitted line. The values of $C_p°$ and $S°$ were obtained from Phillips et al.[25] for the 17 anions F^-, Cl^-, Br^-, I^-, NO_3^-, ClO_4^-, OH^-, HCO_3^-, IO_3^-, $H_2PO_4^-$, HSO_4^-, CO_3^{2-}, HPO_4^{2-}, SO_4^{2-}, PO_4^{3-}, $Fe(CN)_6^{3-}$, and $Fe(CN)_6^{4-}$.

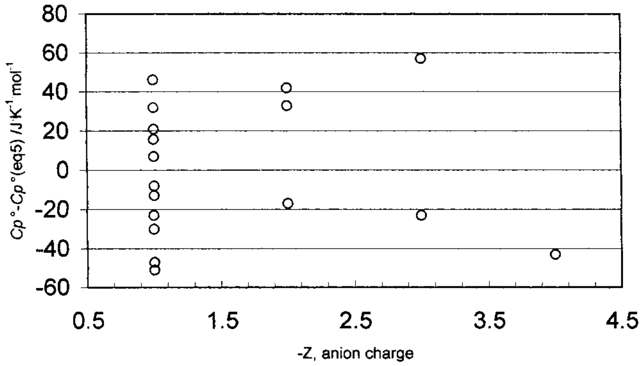

Figure 4. Deviation plot of the arithmetic difference ($C_p° - C_p°$(eq 5)) versus anion charge, $-z$. Values of $C_p°$ are identical to those used in Figure 3. The deviations are indicative of random errors.

propagated as the square root of the sum of the squares of the individual uncertainties, with the assumption that the errors are random.[32] The value of the standard heat capacity for S^{2-}, $C_p° = (-284 \pm 60)$ J·K^{-1}·mol^{-1}, was obtained from the correlation[25] in eq 5. The coefficients for

$$C_p°/\text{J·K}^{-1}\text{·mol}^{-1} = -7.14 - 133.15z + {}^2/_3 S°/\text{J·K}^{-1}\text{·mol}^{-1} \quad (5)$$

eq 5 were obtained from a fitting of seventeen pairs of values for $C_p°$ and $S°$, for 17 selected anions. Figure 3 is a plot of the calculated difference ($C_p° - {}^2/_3 S°$) for the anions versus anion charge, $-z$, after linear regression with LINEST. The slope of the plot is −133.15 J·K^{-1}·mol^{-1}, with a standard error of 9.50, and the intercept is −7.14 J·K^{-1}·mol^{-1}, with a standard error of 17.40. The coefficient of determination is $R^2 = 0.929$, indicative of a close fitting of the data to a straight line. Figure 4 is a plot of the difference ($C_p° - C_p°$(eq 5)) versus anion charge, $-z$. $C_p°$ is the value of the standard heat capacity for each anionic species used to develop eq 5, while $C_p°$(eq 5) is the value calculated from the correlation in eq 5. It can be seen that there are eight differences above the ideal zero line and nine below the line. This virtually equal distribution is interpreted as an absence of a dependence of the difference between the standard heat capacities and their fitted values on the charge of the anion. On the basis of this plot, an estimated error of ±60 J·K^{-1}·mol^{-1} is assigned to the standard heat capacity for S^{2-} that has been calculated with eq 5. The change in heat capacity at 25 °C and infinite dilution for eq 1 from this $C_p°$ and the $C_p°$ value[31] for HS^- in Table 3 is $\Delta C_{p,2a} = (-192 \pm 60)$ J·K^{-1}·mol^{-1}.

Stephens and Cobble[13] calculated $C_p° = (-439 \pm 38)$ J·K^{-1}·mol^{-1} on the basis of the value of $C_p° = 130$ J·K^{-1}·mol^{-1} for the H^+ ion. If $C_p° = 0$ for H^+, then $C_p° = -309$ J·K^{-1}·mol^{-1} for S^{2-}. This value of the standard heat capacity of S^{2-} compares reasonably well with $C_p° = -284 \pm 60$ J·K^{-1}·mol^{-1} calculated from the correlation in eq 5.

The effect of the magnitude of the derivative of the heat capacity on $R \ln K_{2a}$ can be estimated by rewriting eq 3 in the equivalent form,[10] eq 6. According to eq 6, when the

$$R \ln K_{2a} = -\Delta G_{2a}^{\ominus}/\theta + \Delta H_{2a}^{\ominus}[(1/\theta) - (1/T)] + \Delta C_{p,2a}^{\ominus}[(\theta/T) - 1 + \ln(T/\theta)] + (\theta/2)(d\Delta C_{p,2a}/dT)^{\ominus}[(T/\theta) - (\theta/T) - 2\ln(T/\theta)] \quad (6)$$

derivative of the heat capacity of dissociation is zero, the values of $R \ln K_{2a}$ depend on the temperature with a linear term in $1/T$ and an additional nonlinear term in temperature multiplied by the heat capacity. The effect of both terms on $R \ln K_{2a}$ reflects the magnitude of both $\Delta H_{2a}^{\ominus}$ and $\Delta C_{p,2a}^{\ominus}$. The dependence of $R \ln K_{2a}$ on the derivative of the heat capacity can be estimated by examination of the nonlinear temperature term of the heat capacity derivative. The values of this term as a function of increasing temperature were calculated from 25 °C up to 325 °C and are represented as the curve in Figure 5. The magnitude of this term for the heat capacity derivative in eq 6 is seen to increase in a nonlinear manner with increasing temperature. Furthermore, the few literature values of an estimated heat capacity derivative for reactions involving aqueous sulfur species[31,33] are $< \pm 3$ J·K^{-2}·mol^{-1}. It is concluded that the magnitude of the term containing the

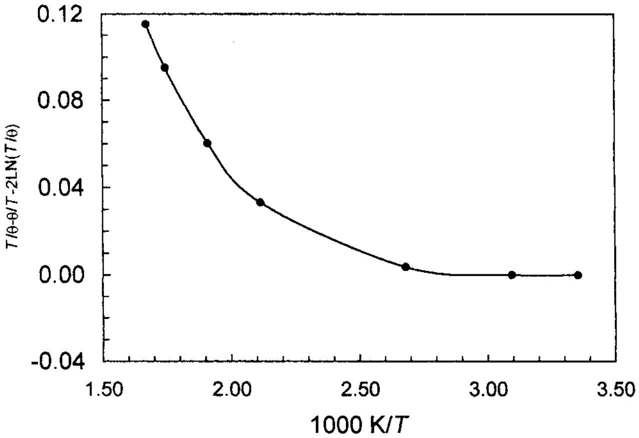

Figure 5. Increase in the magnitude of the temperature dependence of the derivative of the heat capacity, the third term in eq 6, with increasing temperature. The reference temperature is $\theta = 298.15\ T$/K.

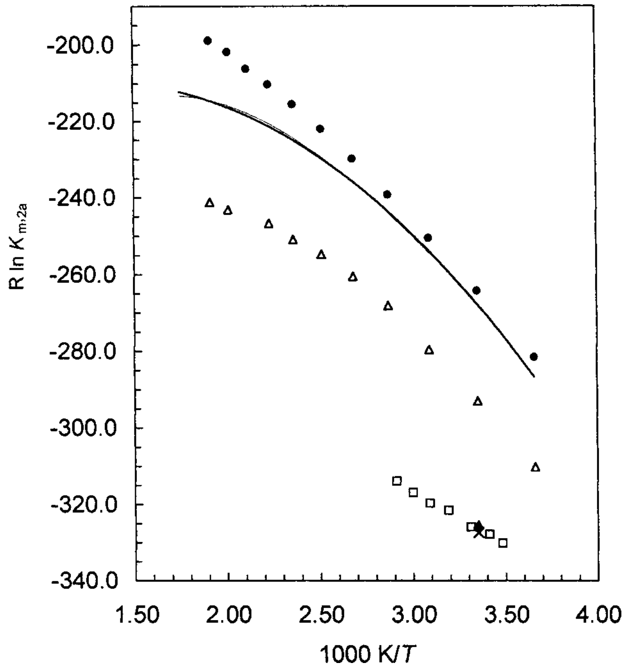

Figure 6. Variation in $R \ln K_{m,2a}$ from 0 °C (1000 K/T = 3.66) to 300 °C (1000 K/T = 1.74). Symbols: (—) $R \ln K_{2a}$, computed with eq 3 from the standard thermodynamic data in Table 3; (□) Giggenbach,[15] 14 mol·L^{-1} NaOH; (×) Licht et al.,[16] (up to 18) mol·L^{-1}; (▲) Meyer et al.,[17] 16.9 mol·L^{-1} NaOH; (●) $R \ln K_{2a}$ computed from eq 18, in Stephens and Cobble;[13] (△) Dickson,[24] 1 p/MPa (10 bar), in sulfide solutions.

derivative of the heat capacity for eq 1 can be considered negligible up to about 300 °C (1000 K/T = 1.74), for the purpose of predicting the variation in $R \ln K_{2a}$ from 0 °C up to this temperature.

Predicted Variation in $R \ln K_{2a}$ up to 300 °C

Figure 6 represents four consistent sets of K_{2a}'s. The first set is the line calculated from the standard thermodynamic values in Table 3 for the aqueous species HS^- and S^{2-}, computed with eq 6 from (0 to 300) °C at 25 °C intervals with Excel Virtual Basic for Applications.[26] According to this plot, $R \ln K_{2a}$ becomes increasingly more positive in a nonlinear manner up to about 1000 K/T = 2.01 (225 °C), with an obvious change in slope to 1000 K/T = 1.74 (300 °C). The second and most negative set is a plot of smoothed $R \ln K_{m,2a}$ in 14 mol·L^{-1} NaOH estimated from Figure 6 in Giggenbach,[15] from Licht et al.[16] in up to 18 mol·L^{-1} solutions, and from Meyer et al.[17] in solutions that contain 16.9 mol·L^{-1} NaOH. The large differences in $R \ln K_{2a}$ can be attributed to the effects of a high hydroxide concentration, compared to the calculated values at infinite dilution for the first set. Plots of the data at 1 MPa from Dickson[24] show a trend toward increasingly positive $R \ln K_{2a}$ with temperature, with a shape similar to the calculated plot. The fourth curve is a plot of smoothed values calculated from the equation developed by Stephens and Cobble[13] for use in calculating pK_{2a} up to 250 °C. Their initial values are <5 units of $R \ln K_{2a}$ more positive than those computed with eq 3 and become increasingly more positive with a barely perceptible bending at the higher temperatures. It is seen that the shapes of the plots at higher temperatures differ by ~15 $R \ln K_{2a}$ units at 250 °C.

The effect of increasing saturation vapor pressure for temperatures above 100 °C has not been taken into account in the calculation of values of K_{2a}. All experimental values of log K_{2a} were obtained from data up to 90 °C. This temperature range corresponds to a pressure of about 0.101 MPa. However, saturation vapor pressures become significantly higher, as the temperature increases above 100 °C.

Standard Reduction Potential for Sulfur

The standard reduction potential at 25 °C and at infinite dilution for eq 7 calculated from the standard Gibbs energy

$$\mathrm{S(rhomb)} + 2\mathrm{e} \rightarrow \mathrm{S}^{2-} \qquad (7)$$

data in Table 3 and $\Delta G = -nFE$, where $n = 2$ and F = 96 485.3 C·mol^{-1}, is $E^\ominus$ = (−0.476 ± 0.004) V. This potential compares exactly with the published[34] $E^\ominus$ = −0.476 V. However, Zhdanov,[35] apparently on the basis of a value of $\Delta_f G^\circ$ = 86.31 kJ·mol^{-1} for the S^{2-} ion, has tabulated E = − 0.447 V, a difference of −0.029 V.

Conclusions

The goal of this work was to obtain unequivocal standard thermodynamic values for the aqueous species S^{2-} that could be used with confidence, by fitting consistent laboratory measurements of K_{2a} at infinite dilution to eq 3. Unfortunately, the experimental data are not sufficiently consistent to permit direct computation of $\Delta_f H^\circ$, S°, $C_p{}^\circ$, and $(d\Delta C_p/dT)^\circ$ by fitting the data to CGCALC. The standard thermodynamic values for the aqueous species S^{2-} at saturation vapor pressure, 25 °C, and I = 0 mol·kg^{-1} are summarized in Table 3. These values are consistent with the equation $\Delta G_{2a}{}^\ominus = \Delta H_{2a}{}^\ominus - 298.15\Delta S_{2a}{}^\ominus$ to within ±0.1 kJ·mol^{-1}. While additional experimental data are needed, the three plots in Figure 1 do follow straight lines, in obedience to the theoretical prediction of the Debye–Hückel equation, eq 4. It is concluded that the standard thermodynamic data for S^{2-} in Table 3 are a reasonable interpretation of the published data for eq 2 and that measurements in very high hydroxide concentrations are valid for these high concentrations but cannot be compared with data calculated to the standard condition of infinite dilution.

The larger question on values of K_{2a} has been discussed for at least 30 years.[9] Ellis and Giggenbach[36] suggested ignoring S^{2-} in favor of calculation with HS^- for obtaining the solubility product of metal sulfides. This ignoring of the species S^{2-} is the apparent rationale for calculating solubility products for metal sulfides from the equation[37] $MS + 2H^+ = M^{2+} + H_2S(aq)$, instead of the expected $MS = M^{2+} + S^{2-}$. In addition, the effect of S^{2-} has been considered relatively unimportant in understanding corrosion processes in power plants,[38] for data involving water pollutants,[39] and in the study of natural resources that contain sulfides.[31] The results of this work provide a basis for the use of a standard value of $K_{2a}^{\ominus}$ for these diverse applications, to high temperatures.

New experimental data calculated to zero ionic strength are needed at all temperatures. The enthalpy of neutralization calculated with the data in Table 3 is $\Delta H_{2b}^{\ominus} = -1.005\ \text{kJ}\cdot\text{mol}^{-1}$. Alternatives to measuring K_{2b} and $\Delta H_{2b}^{\ominus}$ with such low values should be examined, for example[32] titration with $Fe(CN)_6^{3-}$. The resulting equilibrium constants could then be used to calculate standard thermodynamic values for S^{2-} and subsequently values of K_{2a}. Thermodynamic analysis makes heavy use of numerical calculations, so that computer assistance is mandatory. While present methods can be quick and accurate, future software should extract apparent equilibrium constants from both computer databases and text in research publications, tabulate experimental values, reject inconsistent data, calculate the equilibrium constants to a standard zero ionic strength at all temperatures, fit these to a theoretical model, print out and plot the best values, compare these with the input and other data, print out tables of recommended values, and, for commercial applications, improve the mathematical model for simulating chemical reactions in high temperature aqueous media.

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