Thermodynamics of Solution of SO₂(g) in Water and of Aqueous Sulfur Dioxide Solutions

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A consistent set of thermochemical property values, $\Delta_f H°$, $\Delta_f G°$, $S°$, and $C_p°$, at 298.15 K is given for the known constituents of aqueous sulfur dioxide (SO_2^0(aq), HSO_3^-(aq), SO_3^{2-}(aq), H^+(aq), and $S_2O_5^{2-}$(aq)). Also tabulated are values of the mean ionic activity coefficients, osmotic coefficients, partial pressure of SO_2(g), and the relative apparent molar enthalpy as a function of concentration of SO_2(aq) at 298.15 K. The data analysis considered a wide variety of measurement techniques: calorimetric enthalpies of solution and reaction, heat capacities, equilibrium constants, solubilities, and vapor pressure measurements, both partial and total, over aqueous solutions of SO_2 for the temperature range 278 to 393 K. All auxiliary data have been taken from the most recent set of CODATA values which were converted to a standard state pressure of one bar (0.1 MPa). For the process SO_2(g)$=SO_2^0$(aq), the selected "best" values are: $K=1.23\pm0.05$ mol kg⁻¹ bar⁻¹, $\Delta G° = -0.51\pm0.10$ kJ mol⁻¹, $\Delta H° = -26.97\pm0.30$ kJ mol⁻¹, and $\Delta C_p° = 155\pm10$ J mol⁻¹ K⁻¹. The standard state partial molar entropy of SO_3^{2-}(aq), obtained by the analysis of data via two independent thermodynamic pathways is -15.40 ± 0.80 J mol⁻¹ K⁻¹ at 298.15 K. Parameters are given which extend the predictions to temperatures up to 373 K.

Key words: bisulfite; calorimetry; enthalpy; entropy; Gibbs energy; heat capacity; pyrosulfite; solubility; sulfite; sulfur dioxide; thermodynamic data; vapor pressure; water.

1. Introduction

The purpose of this paper is to present the results of an analysis of the thermodynamic properties of the $SO_2 + H_2O$ system. This study was performed as part of the analysis of the thermodynamics of sulfur and its compounds. The aqueous species of relevance to this study are neutral aqueous sulfur dioxide SO_2^0(aq), bisul-

fite ion HSO_3^-(aq), sulfite ion SO_3^{2-}(aq), pyrosulfite ion $S_2O_5^{2-}$(aq), and H^+(aq). A consistent set of property values[1], $\Delta_f H°$, $\Delta_f G°$, $S°$, and $C_p°$ at 298.15, is given for these species which results from the evaluation of the various processes involving them. Also included are values of the activity and osmotic coefficients, the relative apparent molar enthalpy (L_ϕ) as a function of concentration, and the partial pressure of SO_2(g) over its aqueous solution.

Throughout this paper we are adhering to the standard states and units used in the NBS Tables of Chemical Thermodynamic Properties [1][2]. All auxiliary thermochemical data have been taken from the most recent set of CODATA key values [2] which were converted,
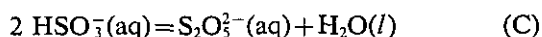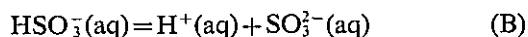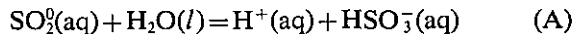
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[1] See Glossary of symbols at end of paper.

[2] Figures in brackets indicate literature references.

where appropriate, to a standard state pressure of one bar (0.1 MPa).

Thermodynamic data from a wide variety of measurement techniques are considered. They include calorimetric measurements of heat capacities and enthalpies of solution and reaction, measured equilibrium constants, entropies, solubilities, and vapor pressure measurements (both partial and total) over aqueous solutions. The approach adopted in this paper is to select a tentative set of values and accompanying uncertainties for the various processes involving sulfur (IV)-oxygen species and then to examine the various thermodynamic pathways for consistency. A final set of values for both the processes and thermodynamic properties is then selected which provides a "best" fit to all of the available data. The final uncertainties are adjusted to reflect the agreement or lack of it between the various data sets.

## 2. Key Processes Involved in the Evaluation

The species considered to be present in an aqueous solution of SO_2 (stoichiometric "SO_2(aq)") are neutral, unionized SO_2^0(aq), HSO_3^-(aq), SO_3^{2-}(aq), $S_2O_5^{2-}$(aq), and H^+(aq). They are involved in the following equilibria:

$$SO_2^0(aq) + H_2O(l) = H^+(aq) + HSO_3^-(aq) \qquad (A)$$

$$HSO_3^-(aq) = H^+(aq) + SO_3^{2-}(aq) \qquad (B)$$

$$2\ HSO_3^-(aq) = S_2O_5^{2-}(aq) + H_2O(l) \qquad (C)$$

Selections are made for the various parameters that enter into the solution process of SO_2(g) into water so that a set of "best" values of ΔG° and ΔH° can be obtained for the processes:

$$SO_2(g) = SO_2^0(aq) \qquad (D)$$

$$SO_2(g) + H_2O(l) = H^+(aq) + HSO_3^-(aq) \qquad (E)$$
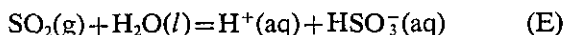
The standard state partial molar entropy of SO_3^{2-}(aq) can be obtained from the standard state Gibbs energy and enthalpy changes for the process:

$$SO_2(g) + H_2O(l) = 2\ H^+(aq) + SO_3^{2-}(aq) \qquad (F)$$
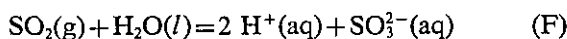
which is the summation of processes (A), (B), and (D). This partial molar entropy can also be obtained independently using the data for the process:

$$Na_2SO_3(cr) = 2\ Na^+(aq) + SO_3^{2-}(aq) \qquad (G)$$
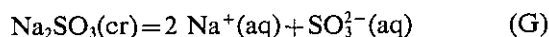
together with the Third Law entropy for Na_2SO_3(cr), the enthalpy of solution, and the value of ΔG° for the solution process (G).

3. Equilibrium Calculations on Aqueous Solutions of Sulfur Dioxide

The equilibrium constants for the equilibria in aqueous solutions of SO_2 as described in processes (A), (B), and (C) are:

$$K_A = [\hat{a}\{H^+(aq)\}\ \hat{a}\{HSO_3^-(aq)\}]$$
$$\div [\hat{a}\{SO_2^0(aq)\}\ \hat{a}\{H_2O(l)\}] \qquad (1)$$

$$K_B = \hat{a}\{H^+(aq)\}\ \hat{a}\{SO_3^{2-}(aq)\}/\hat{a}\{HSO_3^-(aq)\} \qquad (2)$$

and

$$K_C = \hat{a}\{S_2O_5^{2-}(aq)\}\ \hat{a}\{H_2O(l)\}$$
$$\div \hat{a}^2\{HSO_3^-(aq)\}. \qquad (3)$$

In the above equations, $\hat{a}_i$ is the activity of the ith species which is equal to the quantity $\hat{m}_i\hat{\gamma}_i$ where $\hat{m}_i$ and $\hat{\gamma}_i$ are, respectively, the molality and activity coefficient of that species. The symbol " ^ " denotes a quantity which pertains to a species as distinct from a stoichiometric quantity [3]. The absence of the symbol " ^ " over a quantity implies that the quantity is stoichiometric. The treatment of the experimental data often requires some assumptions about the activity coefficients of the species in solution and the mathematical solution of these three simultaneous, nonlinear equations for the molalities of all of the species considered to be present in solution. The first requirement will now be addressed.

Since we have no direct knowledge of the activity coefficients of these or any other individual aqueous charged species, it is necessary to make assumptions to obtain values for these activity coefficients. It is assumed that the activity coefficients can be calculated using the expression:

$$\ln \hat{\gamma}_i = -A_m \hat{I}^{1/2}\hat{z}_i^2/(1 + B\ \hat{I}^{1/2}) \qquad (4)$$

where A_m is the Debye-Hückel constant, B is an "ion-size" parameter, and $\hat{I}$ is the ionic strength which is calculated as:

$$\hat{I} = (1/2)\Sigma \hat{m}_i \hat{z}_i^2. \qquad (5)$$

The above summation extends over all of the species in the solution. The Debye-Hückel constants tabulated by Clarke and Glew [4] were used in our calculations. Staples and Beyer [5] have recently calculated values of the Debye-Hückel limiting slopes using the IAPS recommended values for the dielectric constants and density of water as a function of temperature [6,7]. These new limiting slopes differ by 0.24 and 0.61%, respectively, from the Gibbs energy and enthalpy limiting slopes given by Clarke and Glew [4]. The effect on our final recommended values due to uncertainties in the Debye-Hückel slopes is negligible in comparison with the experimental errors in measured properties which were extrapolated to zero ionic strength whenever possible.

The B parameter in eq [4] is a quantity which serves to account for the repulsive forces between the particles. If sufficiently accurate activity or osmotic coefficients were available for aqueous solutions of SO_2, it would be possible to regress a value for this parameter using a chemical equilibrium model [3]. Since this information is not available, it is necessary to work with estimated or inferred values of B. Evidence for a value of B equal to 1.5 was obtained when extrapolating measured values of K_A (sec. 4.1) to zero ionic strength; specifically, the extrapolation could frequently be made with a line of lesser slope when a value of 1.5 for B was used to calculate values of $\hat{y}_i$. Also, a B value of 1.5 is typical of the values obtained by Hamer and Wu [8] from their correlation of the activity and osmotic coefficient data of aqueous uni-univalent electrolytes. Evidence for a value of B equal to 2.5 was found in the treatment of the heat of solution and heat of dilution data (sec. 4.2) to obtain values of ΔH_A°. There the best fit of the experimental data was frequently obtained using a value of B equal to 2.5. Less direct evidence for a value of 2.5 comes from a treatment of the osmotic coefficients of aqueous sulfuric acid using an equilibrium model [3] in which it was found that a value of B equal to 2.5 could represent the osmotic coefficients of sulfuric acid to within 1.2% up to a stoichiometric molality of 0.20 mol kg^{-1}. This stoichiometric molality corresponds to a calculated (see eq (5)) (species) ionic strength of 0.25 mol kg^{-1}. Since an aqueous solution of SO_2 with a stoichiometric molality of 2.0 mol kg^{-1} has a calculated ionic strength of only 0.21 mol kg^{-1}, the use of assumed values of B ranging from 1.5 to 2.5 will allow us to proceed with the necessary equilibrium calculations without serious error.

The solution of the simultaneous, nonlinear equations (1), (2), and (3) was accomplished using an iterative numerical procedure (CO5NCF) which is a part of a library of numerical analysis programs [9]. The calculation was made self-consistent both in regards to the activity of the water which is a participant in the equi-

ilibria (see reference [3]) and with eqs (4,5). This model allows us to calculate the amounts of each species in the solutions and values of the fractions (α_i) of the species, i.e., $\alpha_i = \hat{n}_i / m^{st}$ where m^{st} is the stoichiometric amount of SO_2 in solution calculated as $m^{st}(H_2SO_3)$ for convenience. It does not imply the physical existence of H_2SO_3. Results of these calculations at 298.15 K are given in table 1 using our final selected values of K_A, K_B, and K_C and a value of B equal to 2.0.

Throughout, where necessary and possible, reported equilibrium constants have been corrected to 298.15 K, for the activity, and to zero ionic strength.

4. The Thermodynamic Parameters for the Description of the Equilibria in Solution at 298.15 K and as a Function of Temperature

4.1 Process (A)

The reported equilibrium constants at 298.15 K for process (A), the first ionization of $SO_2^0(aq)$, are summarized in table 2a. The most detailed investigations cited are those of Tartar and Garretson [15] and Huss and Eckert [24]. While previous critical evaluations [1,32] have relied upon the results of Tartar and Garretson [15], we have selected the data of Huss and Eckert [24], $K_A = 0.0139 \pm 0.004^a$ mol kg^{-1}, as being preferable since it is based upon two different measurement techniques (conductivity and ultraviolet spectrophotometric measurements) which avoid the possible systematic errors inherent in the use of electrochemical cells which were used by Tartar and Garretson [15].

Measurements of K_A as a function of temperature have been used to obtain values of ΔH_A° which are corrected to 298.15 K (see table 1) using the model of Clarke and Glew [33]. A value of $\Delta C_p^\circ = -272 \pm 10$ J mol^{-1} K^{-1} for process (A) was used in performing these calculations. This heat capacity change is based upon the calorimetrically determined standard state heat capacities of $SO_2^0(aq)$ and $HSO_3^-(aq)$ of, respectively, 195 ± 10 J mol^{-1} K^{-1} (Barbero et al. [34]) and -2 ± 10 J mol^{-1} K^{-1} (Allred et al. [35]). The uncertainties assigned to the calculated enthalpies in table 1b are purely statistical and refer to 95% confidence limits.

The model of Clarke and Glew [33] is based upon a Taylor series expansion of the heat capacity at a reference temperature (298.15 K). When dAC_p°/dT is constant over the temperature range of interest, the

$m^{st}(SO_2)$	$m^{st}(H_2SO_3)$ mol kg^{-1}	$\alpha(H^+)$	$\alpha(HSO_3^-)$	$\alpha(SO_3^{2-})$	$\alpha(SO_2^0)$	$2\alpha(S_2O_5^{2-})$	$\hat{I}$ mol kg^{-1}
0.001000	0.001000	0.9406	0.9404	0.7697×10^{-4}	0.0595	0.6058×10^{-4}	0.9407×10^{-3}
0.002000	0.002000	0.8949	0.8947	0.4036×10^{-4}	0.1051	0.1123×10^{-3}	0.1790×10^{-2}
0.003000	0.003000	0.8576	0.8574	0.2781×10^{-4}	0.1424	0.1573×10^{-3}	0.2573×10^{-2}
0.004000	0.004000	0.8261	0.8259	0.2141×10^{-4}	0.1739	0.1971×10^{-3}	0.3305×10^{-2}
0.005000	0.005000	0.7989	0.7986	0.1749×10^{-4}	0.2011	0.2329×10^{-3}	0.3995×10^{-2}
0.006000	0.006001	0.7750	0.7747	0.1485×10^{-4}	0.2250	0.2654×10^{-3}	0.4651×10^{-2}
0.007000	0.007001	0.7537	0.7534	0.1293×10^{-4}	0.2463	0.2952×10^{-3}	0.5277×10^{-2}
0.008000	0.008001	0.7345	0.7342	0.1148×10^{-4}	0.2655	0.3227×10^{-3}	0.5878×10^{-2}
0.009000	0.009001	0.7172	0.7168	0.1034×10^{-4}	0.2828	0.3483×10^{-3}	0.6457×10^{-2}
0.01000	0.01000	0.7013	0.7009	0.9412×10^{-5}	0.2987	0.3723×10^{-3}	0.7016×10^{-2}
0.02000	0.02000	0.5919	0.5913	0.5111×10^{-5}	0.4081	0.5524×10^{-3}	0.1185×10^{-1}
0.03000	0.03001	0.5271	0.5264	0.3589×10^{-5}	0.4729	0.6742×10^{-3}	0.1583×10^{-1}
0.04000	0.04002	0.4823	0.4816	0.2797×10^{-5}	0.5177	0.7670×10^{-3}	0.1932×10^{-1}
0.05000	0.05004	0.4487	0.4479	0.2307×10^{-5}	0.5513	0.8422×10^{-3}	0.2247×10^{-1}
0.06000	0.06006	0.4221	0.4212	0.1972×10^{-5}	0.5779	0.9056×10^{-3}	0.2537×10^{-1}
0.07000	0.07008	0.4003	0.3994	0.1728×10^{-5}	0.5997	0.9605×10^{-3}	0.2807×10^{-1}
0.08000	0.08011	0.3821	0.3810	0.1541×10^{-5}	0.6179	0.1009×10^{-2}	0.3062×10^{-1}
0.09000	0.09014	0.3664	0.3653	0.1393×10^{-5}	0.6336	0.1052×10^{-2}	0.3304×10^{-1}
0.1000	0.1001	0.3527	0.3516	0.1273×10^{-5}	0.6473	0.1092×10^{-2}	0.3535×10^{-1}
0.1500	0.1504	0.3035	0.3022	0.9015×10^{-6}	0.6965	0.1248×10^{-2}	0.4565×10^{-1}
0.2000	0.2007	0.2718	0.2705	0.7065×10^{-6}	0.7282	0.1363×10^{-2}	0.5456×10^{-1}
0.3000	0.3016	0.2318	0.2303	0.5015×10^{-6}	0.7682	0.1532×10^{-2}	0.6987×10^{-1}
0.4000	0.4029	0.2066	0.2049	0.3934×10^{-6}	0.7934	0.1655×10^{-2}	0.8308×10^{-1}
0.5000	0.5045	0.1887	0.1869	0.3260×10^{-6}	0.8113	0.1754×10^{-2}	0.9493×10^{-1}
0.6000	0.6065	0.1751	0.1732	0.2796×10^{-6}	0.8249	0.1836×10^{-2}	0.1058
0.7000	0.7089	0.1643	0.1624	0.2457×10^{-6}	0.8357	0.1906×10^{-2}	0.1159
0.8000	0.8116	0.1554	0.1534	0.2195×10^{-6}	0.8446	0.1968×10^{-2}	0.1254
0.9000	0.9148	0.1480	0.1459	0.1988×10^{-6}	0.8520	0.2023×10^{-2}	0.1344
1.0000	1.0183	0.1416	0.1395	0.1819×10^{-6}	0.8584	0.2072×10^{-2}	0.1430

temperature dependency of the equilibrium constant is given by:

$$R \ln K = -\Delta G^o_{298.15}/298.15 + \Delta H^o_{298.15}(1/298.15 - 1/T)$$
$$+ \Delta C^o_p[(298.15/T) - 1 + \ln(T/298.15)]$$
$$+ (298.15/2)(d\Delta C^o_p/dT)[(T/298.15) -$$
$$(298.15/T) - 2 \ln(T/298.15)] \qquad (6)$$

A convenient aspect of the above equation is that known values of ΔG°, ΔH°, ΔC°_p, and $(d\Delta C^\circ_p/dT)$ at a reference temperature provide all of the information needed to calculate the variation of the equilibrium constant with temperature.

Given in table 2b are enthalpy values obtained from the direct calorimetric measurements of Vanderzee [41], Dobrogowska and Hepler [39], and Zambonin and Jordan [38] and from the enthalpies of solution of $SO_2(g)$ as a function of concentration from the measurements of Johnson and Sunner [37] and Stiles and Felsing [36]. Values of ΔH°_A were also obtained from the heat of dilution measurements of Dobrogowska and Hepler [40]

using a regression calculation in which ΔH°_A was varied in the equilibrium modeling calculation of L_ϕ (sec. 6) until agreement was obtained between measured and calculated values of the heat of dilution. A similar procedure was used for treating the aforementioned enthalpy of solution measurements of $SO_2(aq)$ where values of L_ϕ could be obtained from the concentration dependence of the heat of solution measurements. We adopt a value of $\Delta H^\circ_A = -17.80 \pm 0.40$ kJ mol^{-1} based largely on the direct calorimetric measurements of Dobrogowska and Hepler [39] and of Vanderzee [41] and the enthalpy of solution measurements of Johnson and Sunner [37]. Note that in table 1b the direct calorimetric measurements of Dobrogowska and Hepler [39] and of Vanderzee [41] are sensitive to the B parameter. This causes an uncertainty in the final value of ΔH°_A comparable to the errors in the measurements themselves.

4.2 Process (B)

The thermodynamic data for process (B), the second ionization for $SO_2^0(aq)$, are summarized in table 3.

Table 2. Thermodynamic parameters for process (A): $SO_2^0(aq) + H_2O(l) = H^+(aq) + HSO_3^-(aq)$.

a. Equilibrium constant at 298.15		b. Enthalpy change at 298.15 K		
Investigator(s)	K/mol kg^{-1}	Investigator(s)	$\Delta H°$/kJ mol^{-1}	Method
Drucker [10]	~0.009[a,b]	Stiles and Felsing [36]	−17.2±0.7[a]	calorimetric-heats of solution
Sherill and Noyes [11]	0.012[c]	Johnstone and Leppla [13]	−16.4±0.9	K vs T
Britton and Robinson [12]	~0.008[a]	Johnson and Sunner [37]	−18.0±0.6[a]	calorimetric-heats of solution
Johnstone and Leppla [13]	0.0130[d]	Deveze and Rumpf [19]	−16.7±1.0	K vs T
Yui [14]	0.0127	Flis et al. [20]	−16.7±10.	K vs T
Tartar and Garretson [15]	0.0172	Zambonin and Jordan [38]	−14.3±1.5	calorimetric-heats of solution
Frydman et al. [16]	0.02[a]	Dobrogowska and Hepler [39]	−17.4±0.3[b]	calorimetric-neutralization
Ellis and Anderson [17]	0.014	Dobrogowska and Hepler [40]	−18.2±1.0[a]	calorimetric-heats of dilution
Ludemann and Franck [18]	0.0103[e]	Vanderzee [41]	−17.8₂±0.3[c]	calorimetric-neutralization
Deveze and Rumpf [19]	0.0145			
Flis et al. [20]	0.010			
Deveze [21]	0.013			
Sekine et al. [22]	0.014[a]			
Beilke and Lamb [23]	0.0165[a]			
Huss and Eckert [24]	0.0139			

[a] Corrections were applied.

[b] Drucker's [10] results are based on the measurements of McRae and Wilson [25] and of Walden and Centnerzwer [26].

[c] Based on measurements of Kerp and Bauer [27] and of Lindner [28].

[d] Based on measurements of Campbell and Maass [29] which are also reported in Beazley et al. [30] and Morgan and Maass [31].

[e] Pressure is 0.2 kbar (20 MPa).

[a] These values were obtained by regression calculations. Additional information obtained from these regressions are as follows: Stiles and Felsing [36], (21 points) B=2.5, ΔH_B^0= −27.14±0.10 kJ mol^{-1}. Johnson and Sunner [37], (7 points) B=2.5, ΔH_B^0= −26.90±0.04 kJ mol^{-1}. Dobrogowska and Hepler [40], (21 points) B=2.0 to 2.5. The uncertainties given here refer to two standard deviations as distinct from the overall assigned uncertainties given above.

[b] This value was obtained using the Guggenheim equation with β= −0.2. If an extended Debye-Hückel equation is used with B=2.5, a value of −17.17 kJ mol^{-1} is obtained; if B is set equal to 1.5 then $\Delta H°$= −17.61 kJ mol^{-1}.

[c] This value was obtained using an extended Debye-Hückel equation with B=1.6. If a value of B=3.0 is used, a value of ΔH_A^0 equal to −17.43 kJ mol^{-1} is obtained.

Table 3. Thermodynamic parameters for process (B): $HSO_3^-(aq) = H^+(aq) + SO_3^{2-}(aq)$.

a. Equilibrium constant at 298.15 K		b. Enthalpy change at 298.15 K		
Investigator(s)	$K \times 10^8$/mol kg^{-1}	Investigator(s)	$\Delta H°$/kJ mol^{-1}	Method
Jellinek [42]	500[a]	Arkhipova et al. [45]	−12.1±4.0	K vs T
Kolthoff [43]	~2[b]	Zambonin and Jordan [38]	−5.2±0.8	calorimetric
Britton and Robinson [12]	~4[b]	Hayon et al. [46]	−11.6±3.3	K vs T
Yui [14]	6.3	Teder [47]	−8.0±5.0	K vs T
Tartar and Garretson [15]	6.24	Krunchak et al. [48]	−16.7±6.7	K vs T
Frydman et al. [16]	~10[b]	Allred et al. [35]	−3.6±0.2	calorimetric
Cuta et al. [44]	6.4[b]	Vanderzee [41]	−3.67±0.07	calorimetric
Arkhipova et al. [45]	5.05			
Hayon et al. [46]	6.3			
Teder [47]	7.9			
Krunchak et al. [48]	6.61			

[a] Uncorrected.

[b] Corrections were applied. The Cuta et al. [44] original extrapolation to zero ionic strength led to K=(7.1±0.5)×10^{-8} mol kg^{-1}.

From table 3a we select a value of K_B equal to (6.5±0.5)×10^{-8} mol kg^{-1}. As was done for process (A), values of ΔH_B^0 were calculated from the variation of K_B with temperature using a constant value of ΔC_p^0= −262±14 J mol^{-1} K^{-1} (C_p^0 of $SO_3^{2-}(aq)$= −264±10 J mol^{-1} K^{-1} from Allred et al. [35]) and the Clarke and Glew model. The values of ΔH_B^0 obtained in this way are in sharp disagreement with the recent calorimetric measurements of Allred et al. [35], Vanderzee [41], and Zambonin and Jordan [38].

The calorimetric values are preferred and a value of −3.65±0.10 kJ mol^{-1} is adopted for ΔH_B^0 based on the first two calorimetric values. Thus for process (B) at 298.15 K, the tentative selected values are: K=(6.5±0.5)×10^{-8} mol kg^{-1}. $\Delta G°$=41.02±0.20 kJ mol^{-1}, $\Delta H°$= −3.65±0.10 kJ mol^{-1}, and ΔC_p^0= −262±14 J mol^{-1} K^{-1}. It will later be necessary to modify $\Delta G°$ to 40.94±0.20 kJ mol^{-1} to obtain thermodynamic consistency in a thermodynamic network, resulting in a predicted K_B of (6.72±0.5)×10^{-8} mol kg^{-1}.

4.3 Process (C)

The relatively few available equilibrium data for process (C), the formation of $S_2O_5^{2-}$(aq) from HSO_3^-(aq), are summarized in table 4a. The molar absorbance of $S_2O_5^{2-}$(aq) obtained by Connick et al. [52] was used to calculate values of K_C from the measurement data obtained by the earlier workers [49–51]. A value of $K_C=0.032\pm0.01$ mol^{-1} kg is adopted from the measurements of Connick et al. [52] who also obtained $\Delta H_C^\circ=4.6\pm4.0$ kJ mol^{-1} (table 4). A value of $\Delta C_p^\circ=-21\pm32$ J mol^{-1} K^{-1} is estimated for process (C) based upon an estimate of -100 ± 25 J mol^{-1} K^{-1} for the partial molar heat capacity of $S_2O_5^{2-}$(aq). Thus for process (C) at 298.15 K: $K=0.032\pm0.01$ mol^{-1} kg, $\Delta G^\circ=8.53\pm0.80$ kJ mol^{-1}, $\Delta H^\circ=-4.6\pm4.0$ kJ mol^{-1}, and $\Delta C_p^\circ=-21\pm32$ J mol^{-1} K^{-1}.

5. Vapor-liquid Equilibrium Data and the Henry's Law Constant for SO$_2$

There are two types of vapor-liquid-equilibrium measurements for the SO_2+H_2O system which were considered, namely, total pressure (SO_2+H_2O) measurements and partial pressure (SO_2) measurements. Knowing the total stoichiometric molality of SO_2 in a given solution, eqs (2,3) can be solved for $\hat{m}\{SO_2^0(aq)\}$. If the partial pressure of the SO_2(g) over that aqueous solution is known, the equilibrium constant for process (D), the Henry's Law constant, is calculated as

$$K_D=\hat{a}\{SO_2^0(aq)\}/f\{SO_2(g)\} \qquad (7)$$

In the above equation, the fugacity (f) of the SO_2(g) has been taken to be equal to its pressure and the activity of SO_2^0(aq) equal to its molality, i.e., $a\{SO_2^0(aq)\}=\hat{m}\{SO_2^0(aq)\}=\alpha\{SO_2^0(aq)\}m^{st}$. The latter assumption is consistent with eq (4). The former assumption is justified since (i) calculations showed that the effect of including the fugacities as calculated from available second virial coefficients [53] perturbed the

calculated values of K_D by less than 1.3% up to a stoichiometric molality of 1.0 mol kg^{-1}, (ii) the values of K_D calculated from most of the data sets examined were extrapolated to zero mol kg^{-1}, and (iii) the scatter in the data sets does not justify this small correction.

Values of the Henry's Law constant (K_D) have also been calculated from measurements of total vapor pressures over aqueous SO_2 solutions. To do this calculation, the vapor pressure of the water over these solutions was calculated from the activity of the water using a chemical equilibrium model [3]. The partial pressure of SO_2(g) is obtained from

$$p\{SO_2(g)\}=p(\text{total})-p\{H_2O(g)\} \qquad (8)$$

The Henry's Law constant was then calculated using eq (7). Not considered here are the results of the few investigations summarized by references [54,55] which are of low precision. The Henry's Law constants obtained from the analysis of the data are given in table 5. Values of ΔG° and ΔH° for process (D) were calculated (see table 6) using the Clarke and Glew equation with ΔC_p° fixed at 155 J mol^{-1} K^{-1}.

We believe that the most reliable of the vapor-liquid-equilibrium investigations is that of Rabe and Harris [62]. The reasons are: (i) they measured the partial pressures of SO_2(g) rather than total pressures, (ii) the precision of their measurement is very good, (iii) the ΔH° calculated from their measurements is close to a calorimetrically determined value which will be discussed shortly, and (iv) they took care to minimize systematic errors due to analyses of the gas phase and aqueous solutions and also due to oxidation of the solutions and absorption of CO_2(g). The results of Vosolobe et al. [66], also based on partial pressure measurements, are close to those of Rabe and Harris [62]. We adopt a value of $\Delta G^\circ=-0.51\pm0.10$ kJ mol^{-1} for process (D). This corresponds to a Henry's Law constant of 1.23 ± 0.05 mol kg^{-1} bar^{-1} at 298.15 K. The assigned uncertainty is large enough to overlap with the mean value obtained from all the ΔG° values for process (D) summarized in table 6 which are based upon the partial and total pressure measurements.

Table 4. Thermodynamic parameters for process (C): 2 HSO_3^-(aq)$=S_2O_5^{2-}$(aq)$+H_2O(l)$.

a. Equilibrium constant at 298.15 K		b. Enthalpy change at 298.15 K		
Investigator(s)	K/mol^{-1} kg	Investigator(s)	ΔH°/kJ mol $S_2O_5^{2-}$(aq))$^{-1}$	Method
Golding [49]	~0.02[a]	Hayon et al. [46]	-3.3	K vs T
Arkhipova and Chistyakova [50]	~0.02[a]	Connick et al. [52]	-4.6	K vs T
Bourne et al. [51]	~0.02[a]			
Connick et al. [52]	0.032			

[a] Corrections were applied.

Table 5. Henry's Law constants (K) for process (D): $SO_2(g) = SO_2^0(aq)$.

T/K	K/mol kg^{-1} bar^{-1}
Data of Beuschlein and Simenson [56] at 0.51 g SO_2/100 g H_2O:	
308.75	0.80
314.15	0.71
320.15	0.59
325.15	0.53
335.75	0.38
344.15	0.31
351.75	0.26
358.15	0.23
365.15	0.20
372.15	0.18
378.35	0.16
384.95	0.14
386.15	0.13
Data of Beuschlein and Simenson [56] at 1.09 g SO_2/100 g H_2O:	
299.95	1.30
306.75	0.98
312.55	0.77
317.35	0.67
323.75	0.56
334.75	0.42
340.55	0.38
346.55	0.33
352.35	0.29
359.55	0.25
371.55	0.22
373.75	0.19
379.75	0.17
Data of Beuschlein and Simenson [56] at 4.36 g SO_2/100 g H_2O:	
296.35	1.28
300.35	1.15
303.15	1.03
306.15	0.93
309.15	0.85
311.35	0.79
315.35	0.71
318.35	0.65
321.35	0.60
325.15	0.55
328.45	0.51
331.55	0.47
334.35	0.44
336.15	0.42
340.35	0.38
343.95	0.36
345.55	0.35

T/K	K/mol kg^{-1} bar^{-1}
Data of Beuschlein and Simenson [56] at 7.45 g SO_2/100 g H_2O:	
298.35	1.37
304.55	1.27
307.35	1.14
310.55	1.07
314.15	0.99
317.15	0.91
320.35	0.84
323.55	0.77
327.55	0.69
328.75	0.66
Data of Byerley [57]:	
298.15	1.26
323.15	0.78
Data of Campbell and Maass [29]:	
298.15	1.20
303.15	1.02
313.15	0.75
323.15	0.57
333.15	0.45
343.15	0.36
353.15	0.30
363.15	0.25
373.15	0.21
383.15	0.18
393.16	0.16
Data of Conrad and Beuschlein [58]:	
298.15	1.17
Data of Douabul and Reilly [59]:	
278.97	3.40
283.12	3.03
288.10	2.50
292.98	2.06
298.15	1.73
303.25	1.47
Data of Hudson [60]:	
283.15	2.35
288.15	1.85
293.15	1.54
303.15	1.07
313.15	0.75

T/K	K/mol kg^{-1} bar^{-1}
Data of Hudson [60] cont'd:	
321.15	0.60
333.15	0.44
343.15	0.36
353.15	0.29
363.15	0.25
Data of Johnstone and Leppla [13]:	
298.15	1.20
308.15	0.85
323.15	0.57
Data of Maass and Maass [61]:	
283.15	2.50
289.65	2.00
295.15	1.63
298.15	1.50
300.15	1.38
Data of Morgan and Maass [31]:	
273.15	3.30
283.15	2.16
291.15	1.53
298.15	1.20
Data of Rabe and Harris [62]:	
303.15	1.02
313.15	0.76
323.15	0.58
333.15	0.45
343.15	0.36
353.15	0.30
Data of Tokunaga [63]:	
283.15	2.57
293.15	2.11
303.15	1.46
313.15	1.07
Data of Vosolobe et al. [64]:	
293.15	1.40
303.15	1.07
313.15	0.80
323.15	0.64
333.15	0.53

Table 6. Thermodynamic parameters for process (D), $SO_2(g) = SO_2^0(aq)$, at 298.15 K. ΔC_p^0 was constrained to be equal to 155 J mol^{-1} K^{-1}.

Worker(s)	ΔG°/kJ mol^{-1}	ΔH°/kJ mol^{-1}
Hudson [60]	-0.581 ± 0.029	-27.31 ± 0.29
Maass and Maass [61]	-0.980 ± 0.053	-23.5 ± 1.9
Campbell and Maass [29]	-0.541 ± 0.097	-27.28 ± 0.65
Morgan and Maass [31]	-0.45 ± 0.12	-25.6 ± 2.2
Conrad and Beuschlein [58]	-0.389	
Johnstone and Leppla [13]	-0.435 ± 0.096	-25.7 ± 2.0
Beuschlein and Simenson [56]		
at 0.51 g SO$_2$/100 g H$_2$O:	-0.66 ± 0.15	-30.39 ± 0.98
at 1.09 g SO$_2$/100 g H$_2$O:	-0.74 ± 0.12	-28.99 ± 0.89
at 4.36 g SO$_2$/100 g H$_2$O:	-0.495 ± 0.022	-26.11 ± 0.27
at 7.45 g SO$_2$/100 g H$_2$O:	-0.97 ± 0.15	-22.6 ± 2.4
pooled:	-0.72 ± 0.24	-27.0 ± 3.4
Rabe and Harris [62]	-0.512 ± 0.068	-26.41 ± 0.67
Vosolobe et al. [64]	-0.475 ± 0.075	-22.2 ± 1.2
Tokunaga [63]	-1.26 ± 0.42	$-21.9 \pm 11.$
Douabul and Reilly [59]	-1.367 ± 0.079	-23.8 ± 2.0
Byerley [57]	-0.573	
Grand average[a]	-0.57 ± 0.10	-25.6 ± 1.2

[a] Discarding the results of Douabul and Reilly [59] and of Tokunaga [63].

6. The Calorimetric Enthalpy of Solution of SO$_2$(g) in Water

Enthalpies of solution of SO$_2$(g) in water have been measured several times [28,36,37,65–68]. Roth and Zeumer [68] have summarized the results of the earlier and not very precise investigations by Berthelot [66], Thomsen [65], and Lindner [28]. These early measurements will not be used. Instead, only the measured enthalpies of solution of SO$_2$(g) in water from the more recent investigations by Johnson and Sunner [37], Stiles and Felsing [36], Ramsetter and Hantke [67], and Roth and Zeumer [68] will be considered. The measurements were treated in two different ways. The first used all of the parameters for processes (A), (B), and (C) to calculate [3] values of the excess Gibbs energy (G^{ex}) as a function of temperature from which the excess enthalpy (H^{ex}) was obtained using

$$H^{ex} = G^{ex} - T(\partial G^{ex}/\partial T)_p \qquad (9)$$

The relative apparent molar enthalpy (L_ϕ) is equal to H^{ex}/m^{st}. It is a stoichiometric quantity.

In table 1b values of ΔH_A^0 were obtained from the data of Johnson and Sunner [37], Stiles and Felsing [36], and Dobrogowska and Hepler [40]. These values were obtained using a minimization, or least-squares calculation. As a byproduct of that calculation, values of the B parameter were also inferred.

Using the previously adopted value of $\Delta H_A^0 = -17.80$ kJ mol^{-1} and a value of B equal to 2.0 in the above

procedure for calculating L_ϕ, the enthalpy of solution data were treated to obtain a value of $\Delta H_D^0 = -27.00 \pm 0.30$ kJ mol^{-1}. Figure 1 shows the graphical treatment of the data; the calculations are shown in table 7. To obtain thermodynamic consistency with later calculations, this value is adjusted to -26.97 ± 0.30 kJ mol^{-1}. A value of $\Delta H_E^0 = -44.77 \pm 0.50$ kJ mol^{-1} is obtained.

The above procedure is essentially equivalent to using the experimental heat of solution data at 298.15 K and correcting for the enthalpies of ionization of all of the species. Thus

$$\Delta H_{meas} = \Delta H_D^0 + [1 - \alpha\{SO_2^0(aq)\}][\Delta H_A^0$$
$$+ L_\phi(H^+ \cdot HSO_3^-(aq))] \qquad (10)$$

where $L_\phi(H^+ \cdot HSO_3^-)$ is the relative apparent molar enthalpy for the (hypothetical) solution consisting only of the ions H$^+$(aq) and HSO$_3^-$(aq). This L_ϕ is different than the stoichiometric L_ϕ above. This type of procedure has been used previously by Wu and Young [69]. In eq (10) contributions to the enthalpy of $S_2O_5^{2-}$(aq) and SO_3^{2-}(aq) were neglected since they are negligible in comparison to that from HSO$_3^-$(aq). In applying eq (10) below the electrostatic contribution $[L_\phi(H^+ \cdot HSO_3^-)$ is negligible in comparison to the other terms and was neglected.

An alternative procedure is to use the above relationship (eq (10)) and to plot the experimental enthalpies of solution as a function of α. In such a plot, the slope yields a value of ΔH_A^0 and the intercept at $\alpha = 1$
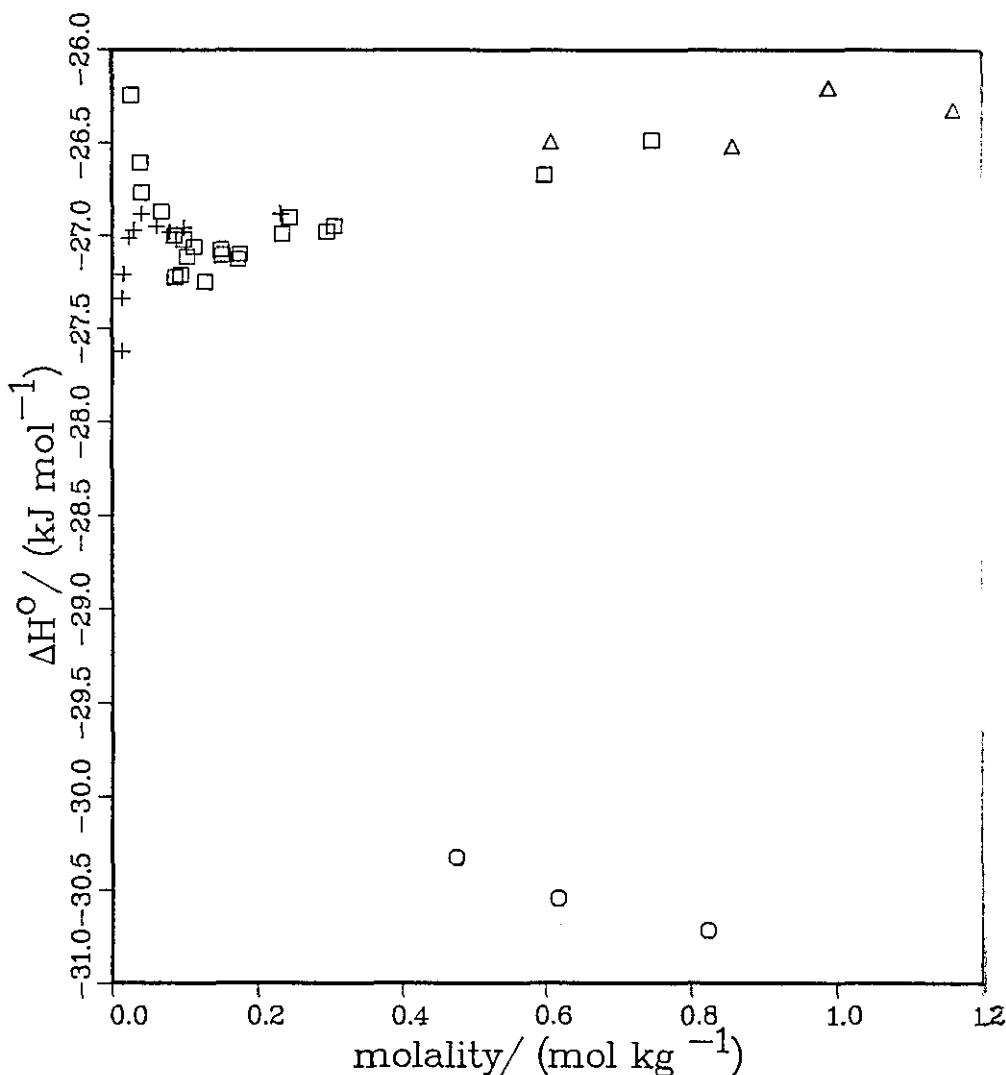
Figure 1-Values of ΔH° at 298.15 for process (D), $SO_2(g) = SO_2^0(aq)$, calculated from the heat of solution measurements of Johnson and Sunner [37] (+), Stiles and Felsing [36] (□), Ramstetter and Hantke [67] (⊃), and Roth and Zeumer [68](Δ). The final selected value of ΔH_D^0 is -26.97 ± 0.30 kJ mol^{-1}.

yields a value of ΔH_D^0.The results of Stiles and Felsing [36] lead to $\Delta H_A^0 = -17.1 \pm 1.2$ kJ mol^{-1} and $\Delta H_D^0 = -27.1 \pm 0.8$ kJ mol^{-1}. The Johnson and Sunner [37] measurements, neglecting the three data points at the lowest concentrations, lead to $\Delta H_A^0 = -18.00 \pm 0.34$ kJ mol^{-1} and $\Delta H_D^0 = -26.76 \pm 0.40$ kJ mol^{-1}. This independent computational method serves as additional confirmation of the correctness of our selected values of ΔH_A^0 and ΔH_D^0. The enthalpies of solution as a function of $\alpha(SO_2^0(aq))$ are shown in figure 2.

7. The Properties of SO_3^{2-}(aq)

The summation of processes (B) and (E) is:

$$SO_2(g) + H_2O(l) = 2H^+(aq) + SO_3^{2-}(aq) \qquad (F)$$
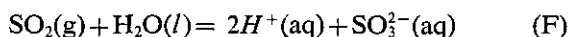
This process is useful for obtaining the thermodynamic properties of SO_3^{2-}(aq).

7.1 The Enthalpy of Process (F)

The enthalpy changes already obtained for processes (B) and (E) lead to a value of $\Delta H_F^0 = -48.42 \pm 0.50$ kJ mol^{-1}. Additional, direct experimental information leading to this enthalpy change is available from measurements on the enthalpy of solution of $SO_2(g)$ in either aqueous NaOH or KOH, represented as:

$$SO_2(g) + 2\,OH^-(aq) = SO_3^{2-}(aq) + H_2O(l) \qquad (F1)$$

Use of the relative apparent molar enthalpy data of Vanderzee and Noll [70] for aqueous Na_2SO_3 and the relative apparent molar enthalpy data tabulated by Parker [71] for aqueous KOH and NaOH leads to values of -164.4 ± 0.23, -162.3 ± 0.30, and -161.1 ± 2.5 kJ mol^{-1} for ΔH_{F1}^0 from the measurement data of Ramstetter and Hantke [67], Roth and Zeumer [68], and

Table 7. Enthalpy of solution data for $SO_2(g)$ in water at 298.15 K. The experimental results (ΔH_{meas}) are given in column six and the corrected results, ΔH° for process (D), are given in column seven. ΔH_R° has been constrained to equal -17.80 kJ mol^{-1}. The B parameter was set at 2.0.

$m^{st}(H_2SO_3)$ mol kg^{-1}	$\alpha(HSO_3^-)$	$\alpha(SO_3^{2-})$	$\alpha(SO_2^0)$	$2\,\alpha(S_2O_5^{2-})$	ΔH_{meas} kJ mol^{-1}	ΔH°

Data of Stiles and Felsing [36]

0.02594	0.5496	0.4074×10^{-5}	0.4497	0.6292×10^{-3}	-35.928	-26.243
0.03839	0.4880	0.2900×10^{-5}	0.5113	0.7533×10^{-3}	-35.196	-26.606
0.04074	0.4789	0.2755×10^{-5}	0.5204	0.7728×10^{-3}	-35.196	-26.767
0.06745	0.4047	0.1785×10^{-5}	0.5943	0.9468×10^{-3}	-33.982	-26.867
0.08470	0.3736	0.1469×10^{-5}	0.6254	0.1029×10^{-2}	-33.560	-26.997
0.08625	0.3711	0.1447×10^{-5}	0.6278	0.1036×10^{-2}	-33.744	-27.223
0.09383	0.3601	0.1346×10^{-5}	0.6389	0.1067×10^{-2}	-33.535	-27.210
0.09778	0.3547	0.1300×10^{-5}	0.6442	0.1083×10^{-2}	-33.250	-27.020
0.1020	0.3493	0.1254×10^{-5}	0.6496	0.1099×10^{-2}	-33.246	-27.112
0.1118	0.3377	0.1159×10^{-5}	0.6612	0.1134×10^{-2}	-32.987	-27.058
0.1273	0.3218	0.1038×10^{-5}	0.6771	0.1183×10^{-2}	-32.895	-27.247
0.1485	0.3036	0.9108×10^{-6}	0.6951	0.1243×10^{-2}	-32.401	-27.073
0.1504	0.3022	0.9015×10^{-6}	0.6965	0.1248×10^{-2}	-32.405	-27.102
0.1728	0.2866	0.8015×10^{-6}	0.7121	0.1303×10^{-2}	-32.154	-27.127
0.1754	0.2849	0.7914×10^{-6}	0.7137	0.1309×10^{-2}	-32.095	-27.097
0.2334	0.2549	0.6219×10^{-6}	0.7436	0.1425×10^{-2}	-31.459	-26.990
0.2435	0.2507	0.6002×10^{-6}	0.7478	0.1442×10^{-2}	-31.296	-26.901
0.2947	0.2324	0.5112×10^{-6}	0.7660	0.1522×10^{-2}	-31.049	-26.976
0.3050	0.2293	0.4967×10^{-6}	0.7692	0.1536×10^{-2}	-30.966	-26.948
0.5983	0.1742	0.2828×10^{-6}	0.8240	0.1829×10^{-2}	-29.719	-26.669
0.7461	0.1589	0.2354×10^{-6}	0.8391	0.1929×10^{-2}	-29.263	-26.482

Data of Ramstetter and Hantke [67]

0.4744	0.1917	0.3432×10^{-6}	0.8066	0.1726×10^{-2}	-33.681	-30.324
0.6160	0.1721	0.2760×10^{-6}	0.8260	0.1843×10^{-2}	-33.556	-30.543
0.8223	0.1526	0.2171×10^{-6}	0.8454	0.1974×10^{-2}	-33.388	-30.718

Data of Roth and Zeumer [68]

0.6066	0.1732	0.2796×10^{-6}	0.8249	0.1836×10^{-2}	-29.522	-26.490
0.8566	0.1500	0.2099×10^{-6}	0.8480	0.1992×10^{-2}	-29.142	-26.517
0.9876	0.1413	0.1866×10^{-6}	0.8566	0.2058×10^{-2}	-28.673	-26.201
1.1587	0.1321	0.1635×10^{-6}	0.8658	0.2133×10^{-2}	-28.543	-26.320

Data of Johnson and Sunner [37]

|						
0.01330	0.6566	0.7401×10^{-5}	0.3430	0.4417×10^{-3}	-39.212	-27.623
0.01416	0.6466	0.7003×10^{-5}	0.3529	0.4579×10^{-3}	-38.752	-27.340
0.01544	0.6328	0.6489×10^{-5}	0.3667	0.4807×10^{-3}	-38.376	-27.209
0.02272	0.5708	0.4626×10^{-5}	0.4286	0.5895×10^{-3}	-37.074	-27.013
0.02932	0.5301	0.3706×10^{-5}	0.4692	0.6670×10^{-3}	-36.309	-26.970
0.03964	0.4830	0.2854×10^{-5}	0.5162	0.7639×10^{-3}	-35.384	-26.882
0.06039	0.4204	0.1986×10^{-5}	0.5787	0.9076×10^{-3}	-34.342	-26.950
0.07829	0.3842	0.1590×10^{-5}	0.6148	0.1001×10^{-2}	-33.731	-26.981
0.09772	0.3548	0.1316×10^{-5}	0.6441	0.1083×10^{-2}	-33.187	-26.956
0.2312	0.2559	0.6344×10^{-6}	0.7427	0.1421×10^{-2}	-31.367	-26.881
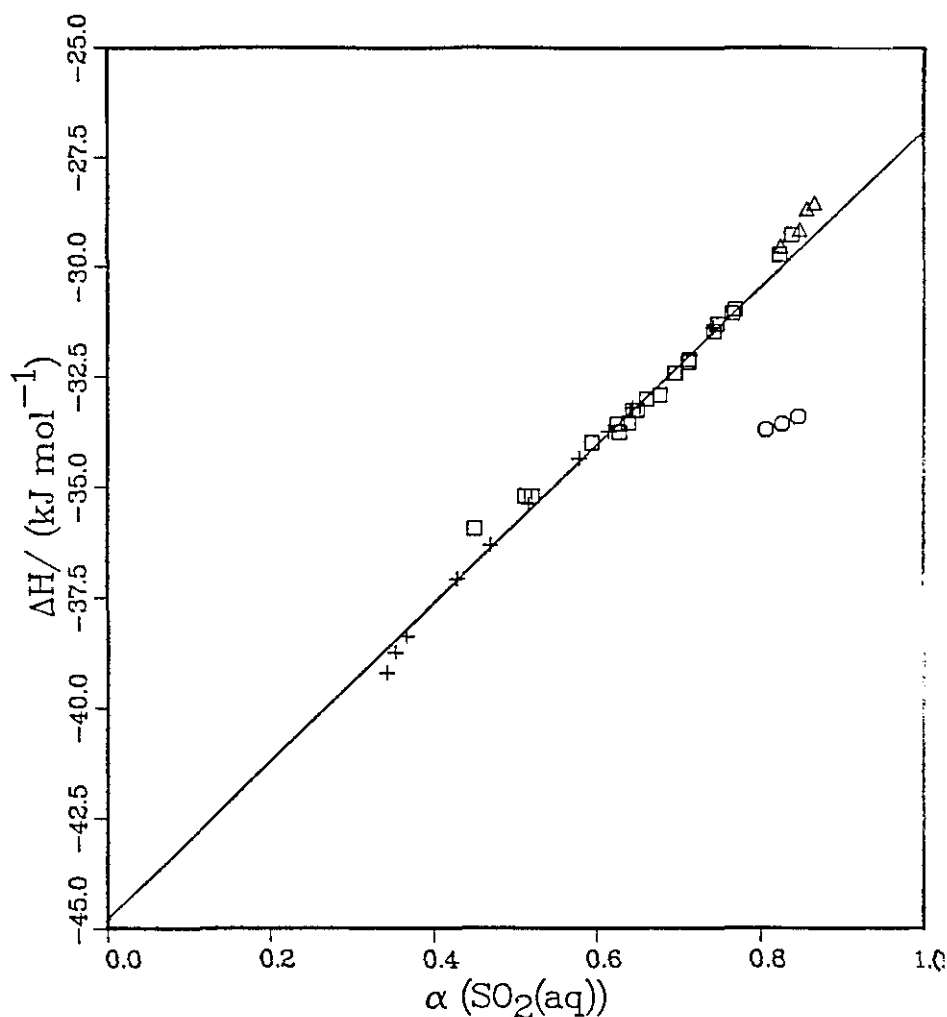
Figure 2-Experimental enthalpies of solution of $SO_2(g)$ in water at 298.15 K as a function of $\alpha(SO_2^o(aq))$. The measurements are those of Johnson and Sunner [37] (+), Stiles and Felsing [36] (□), Ramstetter and Hantke [67] (○), and Roth and Zeumer [68] (△). The straight line connects the selected values of $\Delta H_B^o = -26.97$ and $\Delta H_E^o = -44.77$ k J mol^{-1}.

Zambonin and Jordan [38], respectively. Using the CODATA [2] value of 55.815 ± 0.040 kJ mol^{-1} for the enthalpy of ionization of water, to adjust these respective values of $\Delta H_{F_1}^o$ leads to -52.8 ± 0.25, -50.7 ± 0.32, and -49.5 ± 2.5 kJ mol^{-1} for ΔH_F^o. The uncertainties assigned to the measurements of Ramstetter and Hantke [67] and Roth and Zeumer [68] are purely statistical. These values of ΔH_F^o are given in table 8 together with the value obtained from Zambonin and Jordan's [38] measured enthalpy of solution of $SO_2(g)$ in

Table 8. ΔH^o at 298.15 K for process (F): $SO_2(g) + H_2O(l) = SO_3^{2-}(aq) + 2 H^+(aq)$.

Investigator(s)	ΔH^o/kJ mol^{-1}
Ramstetter and Hantke [67]	-52.8 ± 0.23
Roth and Zeumer [68]	-50.7 ± 0.30
Zambonin and Jordan [38]	-49.5 ± 2.5
Zambonin and Jordan [38][a]	-47.36 ± 0.9
This evaluation	-48.42 ± 0.50

[a] Derived from the authors' measurements of the heat of solution of $SO_2(g)$ in $NaHSO_3(aq)$ and the enthalpy data for processes (A) and (B).

dilute $NaHSO_3$ and their measured values for processes (A) and (B).

It is possible that the result of Ramstetter and Hantke [67] are in error by about 4 kJ mol^{-1} since their enthalpies of solution of $SO_2(g)$ in water (see figs. 1,2) were in error by this amount in the same direction as we believe these are for process (F). We cannot explain the difference of 2.3 kJ mol^{-1} between the ΔH^o for process (F) obtained from Roth and Zeumer [68] and the tentative selection. As can be seen, the results of Zambonin and Jordan [38] bracket this selection. We believe that our selected value is best and needs no serious adjustment. This will become apparent in the next section. A modern, accurate measurement of ΔH^o for process (F1) would be of value in confirming our selection.

7.2 The Standard State Entropy of $SO_3^{2-}(aq)$

7.2.1 From the Tentative Selections for Process (F)

Use of the values of ΔG^o tentatively selected for processes (B) and (E) leads to a value of $\Delta G_F^o = 51.11 \pm 0.24$

kJ mol^{-1}. This value together with $\Delta H_F^o = -48.42 \pm 0.50$ kJ mol^{-1} leads to $\Delta S_F^o = -333.83 \pm 1.9$ J mol^{-1} K^{-1}. The CODATA [2] values for $S^o(H_2O,l)$ (69.950 $\pm$ 0.030 J mol^{-1} K^{-1}) and $S^o(SO_2,g)$ (adjusted to 248.223 $\pm$ 0.05 J mol^{-1} K^{-1} at a standard state pressure of one bar) are then used to calculate a value of -15.66 ± 2.0 J mol^{-1} K^{-1} for the standard state partial molar entropy of SO_3^{2-}(aq).

7.2.2 From Data on the Na$_2$SO$_3$ System

There is a direct path to the standard state partial molar entropy of SO_3^{2-}(aq) from the Third Law entropy of Na$_2$SO$_3$(cr) and the value of ΔG^o and ΔH^o for the process:

$$Na_2SO_3(cr) = 2\ Na^+(aq) + SO_3^{2-}(aq). \qquad (G)$$
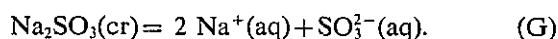
The stable solid phase in equilibrium with saturated Na$_2$SO$_3$ solution at 298.15 K is the heptahydrate. The solubility measurements of Foerster et al. [72] and Kobe and Hellwig [73] lead to a solubility of 2.42 $\pm$ 0.10 mol kg^{-1} at 298.15 K. The activity of water, 0.908 $\pm$ 0.002, and the mean ionic activity coefficient, 0.190 $\pm$ 0.005, at 2.42 mol^{-1} kg^{-1} are obtained by extrapolation of the results of the evaluation of Goldberg [74]. These result in $\Delta G^o = 4.016 \pm 0.20$ kJ mol^{-1} for the process:

$$Na_2SO_3 \cdot 7\ H_2O(cr) = 2\ Na^+(aq) + SO_3^{2-}(aq)$$
$$+ 7\ H_2O(l). \qquad (G1)$$
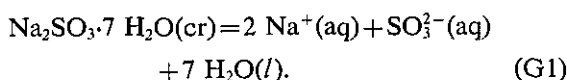
Arii [75] reports vapor pressure measurements over Na$_2$SO$_3 \cdot 7$ H$_2$O(c):

$$\log p(mm\ of\ Hg) = 10.656 - 2797.1/T. \qquad (11)$$

These data, after correction for the nonideality of the water vapor, and with the CODATA ΔG^o value for the vaporization of H$_2$O(l), leads to $\Delta G^o = 4.070 \pm 0.15$ kJ mol^{-1} for the process:

$$Na_2SO_3 \cdot 7\ H_2O(cr) = Na_2SO_3(cr) + 7\ H_2O(l). \qquad (G2)$$
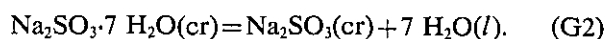
The vapor pressure measurements of Tarassenkow [76] over Na$_2$SO$_3 \cdot 7$ H$_2$O(cr):

$$\log p(mm\ of\ Hg) = 9.949 - 2608/T \qquad (12)$$

were rejected since they lead to an unreasonable ΔS^o for the decomposition process (G2). Combining ΔG_{G1}^o and ΔG_{G2}^o we obtain a value of $\Delta G_G^o = -0.054 \pm 0.25$ kJ mol^{-1} at 298.15 K.
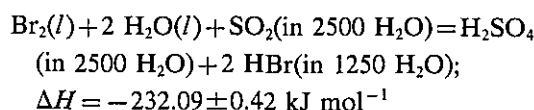
Above 308 K the stable solid phase in equilibrium with an aqueous solution of Na$_2$SO$_3$ is the anhydrous salt. Extrapolation to 298.15 K of the solubility measurements of Foerster et al. [72] and of Kobe and Hellwig [73] leads to a solubility of 3.26 $\pm$ 0.05 mol kg^{-1}. With an exptrapolated [74] mean ionic activity coefficient of 0.19 $\pm$ 0.03, $\Delta G_G^o = 0.13 \pm 0.6$ kJ mol^{-1} is obtained, confirming the result obtained from the pathway involving the heptahydrate.

The recent enthalpy of solution measurements of Vanderzee [41] yield $\Delta H_G^o = -13.26 \pm 0.04$ kJ mol^{-1} and are preferred to the earlier measurements of de Forcrand [77] and Kennedy and Lister [78] which yield $\Delta H_G^o = -14.9 \pm 2.0$ kJ mol^{-1} and -18.62 ± 0.4 kJ mol^{-1}, respectively.
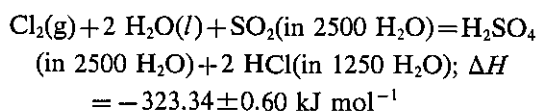
With $\Delta H_G^o = -13.26 \pm 0.04$ kJ mol^{-1} and $\Delta G_G^o = -0.054 \pm 0.25$ kJ mol^{-1} a value of $\Delta S_G^o = -44.29 \pm 0.85$ kJ mol^{-1} is obtained. Use of $S^o\{Na_2SO_3(cr)\} = 145.94 \pm 1.2$ J mol^{-1} K^{-1} at 298.15 K [79] and the CODATA entropy for Na$^+$(aq) of 58.45 $\pm$ 0.15 J mol^{-1} K^{-1}, results in a partial molar entropy of -15.25 ± 1.5 J mol^{-1} K^{-1} for SO_3^{2-}(aq). This value is in very good agreement with the value of -15.66 ± 2.0 J mol^{-1} K^{-1} obtained from the SO$_2$(g) cycle.

8. The Oxidation of SO$_2$(aq) to H$_2$SO$_4$(aq)

There are two calorimetric determinations involving the oxidation of SO$_2$(aq) that were used by the CODATA "Key Values" task group [2] as input for their evaluation of $\Delta_f H^o$ of SO_4^{2-}(aq). Reversing their procedure, we use the final CODATA value of $\Delta_f H^o(SO_4^{2-}(aq)) = -909.34 \pm 0.40$ kJ mol^{-1} and these reactions to obtain $\Delta_f H^o(H_2SO_3(in\ 2500\ H_2O))$. The reactions investigated by Johnson and Sunner [37] and by Johnson and Ambrose [80] are, respectively:

$$Br_2(l) + 2\ H_2O(l) + SO_2(in\ 2500\ H_2O) = H_2SO_4$$
$$(in\ 2500\ H_2O) + 2\ HBr(in\ 1250\ H_2O);$$
$$\Delta H = -232.09 \pm 0.42\ kJ\ mol^{-1}$$

and

$$Cl_2(g) + 2\ H_2O(l) + SO_2(in\ 2500\ H_2O) = H_2SO_4$$
$$(in\ 2500\ H_2O) + 2\ HCl(in\ 1250\ H_2O);\ \Delta H$$
$$= -323.34 \pm 0.60\ kJ\ mol^{-1}$$

Using $\Delta_f H^o$ (HBr(in 1250 H$_2$O)) $= -121.06 \pm 0.15$ kJ mol^{-1} and $\Delta_f H^o$ (HCl(in 1250 H$_2$O)) $= -166.695 \pm 0.10$ kJ mol^{-1} from CODATA [2] and Parker [66] and $\Delta_f H^o$ (H$_2$SO$_4$(in 2500 H$_2$O)) $= -895.43 \pm 0.40$ kJ mol^{-1} from

CODATA and Wu and Young [69] we obtain $\Delta_f H^\circ(SO_2(\text{in } 2500 \text{ } H_2O)) = -333.80 \pm 0.60$ kJ mol^{-1} and -333.82 ± 0.65 kJ mol^{-1}, respectively.

Independently, from the present evaluation we obtain $\Delta_{sol} H = -37.14 \pm 0.20$ kJ mol^{-1} for $SO_2(g) \rightarrow SO_2(\text{in } 2500 \text{ } H_2O)$ which leads to $\Delta_f H^\circ(SO_2(\text{in } 2500 \text{ } H_2O)) = -333.95 \pm 0.28$ kJ mol^{-1}. This agreement, well within the assigned uncertainties, substantiates the selections made here. More importantly, however, the enthalpy relationships between aqueous solutions of SO_2 and $H_2SO_4(aq)$ over a range of concentrations are well defined.

9. Final Selected Values for the Processes and Properties

The very near agreement in the partial molar entropy of $SO_3^{2-}(aq)$ obtained via two independent thermo-chemical pathways may be fortuitous and the result of a cancellation of errors. Nevertheless, it serves to confirm the selections made for the processes used in obtaining the partial molar entropy of $SO_3^{2-}(aq)$. Tables 9 and 10 contain, respectively, our recommended values for the processes and for the thermodynamic properties of the species. These values are consistent with the forthcoming CODATA "Key Values" [2] adjusted to a standard state pressure of one bar. Note that we have adopted a final "best" value of -15.40 ± 0.8 J mol^{-1} K^{-1} for $S^\circ(SO_3^{2-},aq)$ and adjusted the value of K_B to be $(6.7_2 \pm 0.5) \times 10^{-8}$ mol kg^{-1} rather than the value of $(6.5 \pm 0.5) \times 10^{-8}$ mol kg^{-1} used in section 4.2. In tables 9 and 10 the uncertainties have also been adjusted in light of the agreement of the data. The thermodynamic parameters for process (C) are not as well known as those for the other processes. Consequently, the property values for $S_2O_5^{2-}(aq)$ have much larger uncertainties than have been assigned to the other species.

Table 9. Recommended values for the processes involving sulfur(IV)-oxygen species at 298.15 K.

The value of the equilibrium constant for a given process can be calculated using the equation: $R \ln K = -\Delta G^\circ_{298.15}/298.15 + \Delta H^\circ_{298.15}[1/298.15 - 1/T] + \Delta C^\circ_p[(298.15/T) - 1 + \ln(T/298.15)] + (298.15/2)(d\Delta C^\circ_p/dT)[(T/298.15) - (298.15/T) - 2 \ln(T/298.15)]$.

Process		ΔG°	ΔH°	ΔC°_p	$d\Delta C^\circ_p/dT^a$
		kJ mol^{-1}		J mol^{-1} K^{-1}	J mol^{-1} K^{-2}
$SO_3^{2-}(aq) + H_2O(l) = H^+(aq) \pm HSO_3^-(aq)$	(A)	10.60 ± 0.10	-17.80 ± 0.40	$-272. \pm 10$	1.7^a
$HSO_3^-(aq) = H^+(aq) + SO_3^{2-}(aq)$	(B)	40.94 ± 0.20	-3.65 ± 0.10	$-262. \pm 14$	-2.7^a
$2 HSO_3^-(aq) = S_2O_5^{2-}(aq) + H_2O(l)$	(C)^b	8.53 ± 0.80	-4.6 ± 4.0	$-21. \pm 25^a$	-1.9^a
$SO_2(g) = SO_3^{2-}(aq)$	(D)	-0.51 ± 0.10	-26.97 ± 0.30	$155. \pm 10$	-0.035^a
$SO_2(g) + H_2O(l) = H^+(aq) + HSO_3^-(aq)$	(E)	10.09 ± 0.14	-44.77 ± 0.40	$-117. \pm 14$	$+1.7^a$

^{a} Estimated.

^{b} For process (C), all values refer to one mole of $S_2O_5^{2-}(aq)$.

Table 10. Recommended thermodynamic property values at 298.15 K in SI units and at a standard state pressure of one bar (0.1 MPa).

Species	$\Delta_f H^\circ$	$\Delta_f G^\circ$	S°	C°_p
	kJ mol^{-1}		J mol^{-1} K^{-1}	
S(cr, rhombic)	0	0	32.054 ± 0.050^a	22.686 ± 0.050
$SO_2(g)$	-296.81 ± 0.20^a	-300.09 ± 0.21^a	248.223 ± 0.05^a	39.842 ± 0.020
$SO_3^{2-}(aq)$	-323.78 ± 0.32	-300.60 ± 0.23	159.48 ± 0.75	$195. \pm 10$
$S_2O_5^{2-}(aq)$	-973.6 ± 4.1	-808.61 ± 0.94	$154. \pm 13.$	-100.0 ± 25^b
$HSO_3^-(aq)$	-627.41 ± 0.32	-527.14 ± 0.25	134.17 ± 0.65	$-2. \pm 10$
$H_2SO_3^0(aq)^c$	-609.61 ± 0.32	-537.74 ± 0.23	229.43 ± 0.75	$270. \pm 10$
$SO_3^{2-}(aq)$	-631.06 ± 0.40	-486.20 ± 0.33	-15.40 ± 0.80	$-264. \pm 10$
$Na_2SO_3(cr)$	-1098.48 ± 0.42	-1010.08 ± 0.46	145.94 ± 0.80	120.25
Auxiliary Values^a				
$O_2(g)$	0	0	205.152 ± 0.005	29.378 ± 0.003
$H_2(g)$	0	0	130.680 ± 0.005	28.836 ± 0.002
$H_2O(l)$	-285.830 ± 0.04	-237.141 ± 0.04	69.950 ± 0.030	75.300
$Na(cr)$	0	0	51.30 ± 0.20	28.23 ± 0.20
$Na^+(aq)$	-240.34 ± 0.06	-261.95 ± 0.10	58.45 ± 0.15	—

^{a} CODATA [2] selections.

^{b} Estimated.

^{c} Convention, property values are set equal to the sum of those of $SO_2^0(aq)$ and $H_2O(l)$.

The property values given in table 10 for $HSO_3^-(aq)$, $SO_3^{2-}(aq)$, and $S_2O_3^{2-}(aq)$ are based upon a more current data base than are the property values given in earlier evaluations [1,32,81,82]; for this reason they are to be preferred.

Table 11 gives properties ($\gamma_\pm$, ϕ, L_ϕ) and $p(SO_2)$, the partial pressure of $SO_2(g)$ over aqueous solutions of SO_2 as a function of the stoichiometric molality. The values of L_ϕ are obtained as a composite of experimental heat of dilution data [40], heat of solution data [36,37], and the use of the equilibrium model (sec. 6) to calculate values of L_ϕ using the selected property values for processes (A) (B), and (C). The properties $\gamma_\pm$, ϕ, and L_ϕ all have contributions from the various species in the solution. L_ϕ is a bulk, stoichiometric property and is the difference in enthalpy between the real solution and the hypothetical standard state solution consisting of $H^+(aq)$ and $HSO_3^-(aq)$. The activity and osmotic coefficients were calculated using a speciation model of the solution and are expressed in table 11 for the final treatment of aqueous SO_2 solutions as a uni-univalent electrolyte. The excess Gibbs energy is given by $G^{ex} = \nu[m^{st}(H_2SO_3)]RT$

($\ln\gamma_\pm - \phi + 1$), where $\nu = 2$.

Values of $\gamma_\pm$ can also be calculated from the spectroscopic data of Huss and Eckert [24] if one assumes a value of K_A and a value of the B parameter in eq (5) and applies the equation:

$$K_A = [\hat{\gamma}(H^+)\hat{\gamma}(HSO_3^-)]\hat{m}(H^+)\hat{m}(HSO_3^-)]$$
$$\div [\hat{m}(SO_2)a_w] \qquad (13)$$

to calculate the product $[\hat{\gamma}(H^+)\hat{\gamma}(HSO_3^-)]$. Since γ_i^{st} is equal to the quantity $\gamma_i\hat{m}_i/m_i^{st}$, the (stoichiometric) mean ionic activity coefficient ($\gamma_\pm$) can be calculated using:

$$\gamma_\pm = [\gamma(H^+)\hat{\gamma}(HSO_3^-)\hat{m}(H^+)\hat{m}(HSO_3^-)]$$
$$\div [m^{st}(H^+)m^{st}(HSO_3^-)] \qquad (14)$$

The average deviation between the values of $\gamma_\pm$ calculated in this way using the spectroscopic data of Huss and Eckert [24] and the values of $\gamma_\pm$ calculated from the equilibrium model is 0.0026.

Table 11. Stoichiometric thermodynamic properties of aqueous sulfur dioxide solutions at 298.15 K. The values of $\gamma_\pm$, ϕ, and L_ϕ are relative to (H^+) (HSO_3^-).

| $m^{st}(SO_2)$ | $m^{st}(H_2SO_3)$ | $\gamma_\pm$ | ϕ | L_ϕ | $p(SO_2)$ |
mol kg^{-1}				kJ mol^{-1}	bar (0.1 MPa)
0.001000	0.001000	0.909	0.960	1.09	0.0000483
0.002000	0.002000	0.855	0.934	1.91	0.000171
0.003000	0.003000	0.812	0.914	2.58	0.000347
0.004000	0.004000	0.777	0.897	3.14	0.000566
0.005000	0.005000	0.748	0.883	3.61	0.000818
0.006000	0.006001	0.722	0.870	4.05	0.00110
0.007000	0.007001	0.699	0.859	4.43	0.00140
0.008000	0.008001	0.679	0.849	4.78	0.00173
0.009000	0.009001	0.661	0.840	5.08	0.00207
0.01000	0.01000	0.644	0.832	5.36	0.00243
0.02000	0.02000	0.533	0.777	7.36	0.00664
0.03000	0.03001	0.468	0.745	8.54	0.0115
0.04000	0.04002	0.424	0.723	9.36	0.0168
0.05000	0.05004	0.391	0.706	9.99	0.0224
0.06000	0.06006	0.366	0.693	10.46	0.0282
0.07000	0.07008	0.345	0.682	10.85	0.0341
0.08000	0.08011	0.327	0.674	11.17	0.0402
0.09000	0.09014	0.312	0.666	11.44	0.0464
0.1000	0.1001	0.300	0.659	11.66	0.0527
0.1500	0.1504	0.253	0.635	12.56	0.0850
0.2000	0.2007	0.224	0.620	13.14	0.119
0.3000	0.3016	0.188	0.600	13.89	0.188
0.4000	0.4029	0.165	0.588	14.33	0.258
0.5000	0.5045	0.149	0.579	14.64	0.330
0.6000	0.6065	0.137	0.572	14.89	0.403
0.7000	0.7089	0.127	0.566	15.08	0.477
0.8000	0.8116	0.120	0.561	15.24	0.551
0.9000	0.9148	0.113	0.556	15.37	0.625
1.0000	1.0183	0.107	0.553	15.48	0.700

10. The Effects of Perturbations of Parameters on Calculated Quantities in the Equilibrium Modelling of $SO_2 + H_2O$

The model used to describe the $SO_2 + H_2O$ system used several thermodynamic parameters: ΔG°, ΔH°, and ΔC_p° at 298.15 K for processes (A), (B), and (C), and a B parameter (see eq (4)). It is of interest to examine the effects of perturbations in these parameters on the quantities which can be calculated from the model, namely $\alpha(SO_2^0)$, $\gamma_\pm$, ϕ, and L_ϕ. The examination of the effects of these perturbations will be confined to the reference temperature of 298.15 K.

The results of these calculations are summarized in table 12. Each parameter has been perturbed by the limit of error assigned to that parameter in table 9; the B parameter has been perturbed by 0.5. As a result of these calculations, the values of K_A and B are found to be most significant in calculating value of $\alpha(SO_2^0)$, $\gamma_\pm$, and ϕ. In

the calculation of L_ϕ, the most important quantity is ΔH_A° followed by K_A and B.

The results of these calculations are useful in estimating uncertainties in the thermodynamic properties that were calculated from the equilibrium model. Thus the calculated values of K_D are uncertain by at least 1 to 3% because of uncertainties in the calculation of $\alpha(SO_2^0)$. The uncertainties in $\gamma_\pm$, ϕ, and L_ϕ are given in the last column of table 12; uncertainties in $\gamma_\pm$ range from 0.2 to 1.4%, in ϕ from 0.1 to 0.3%, and in L_ϕ from 2 to 3%. This sensitivity analysis does not consider possible coupling effects between the parameters varied.

11. Extension of the Temperature Range Over Which Properties and Equilibrium can be Calculated

In the model used, it was assumed that the heat capacities of the species were independent of temperature. This was necessary since we have no direct knowledge of the temperature dependency of the heat capacities of

Table 12. Percentage effects on calculated quantities $(\alpha(SO_2^0), \gamma_\pm, \phi, \text{ and } L_\phi)$ due to perturbations in the parameters of the model used to describe the thermodynamics of aqueous SO_2 solutions. The parameters which were perturbed were B in eq (4) (1.5 instead of 2.0), K_A (0.0143 instead of 0.0139 mol kg^{-1}), K_B (7.2×10^{-8} mol kg^{-1} instead of 6.7×10^{-8} mol kg^{-1}), K_C (0.042 instead of 0.032), ΔH_A° (-18.20 instead of -17.80 kJ mol^{-1}), ΔH_B° (-3.75 instead of -3.65 kJ mol^{-1}), and ΔH_C° (-8.60 instead of -4.60 kJ mol^{-1}). The temperature is 298.15 K in all cases. A discussion of the effects of the B parameter on the value of ΔH_A° is given in section 4.1.

m mol kg^{-1}	Parameters Modified							total in quadrature
	B	K_A	K_B	K_C	ΔH_A°	ΔH_B°	ΔH_C°	
			Effects on $\alpha(SO_2^0)$					
0.001	-0.08	-2.5	-3.3×10^{-5}	-0.0018	—	—	—	2.5
0.01	-0.34	-1.5	-8.3×10^{-6}	-0.0093	—	—	—	1.5
0.10	-0.50	-0.63	-1.3×10^{-6}	-0.022	—	—	—	0.80
1.00	-0.47	-0.23	-2.0×10^{-7}	-0.035	—	—	—	0.52
			Effects on $\gamma_\pm$					
0.001	-0.044	$+0.16$	-1.7×10^{-5}	-0.00091	—	—	—	0.16
0.01	-0.17	$+0.64$	-3.8×10^{-6}	-0.0047	—	—	—	0.66
0.10	-0.25	$+1.1$	-5.8×10^{-7}	-0.011	—	—	—	1.1
1.00	-0.23	$+1.3$	-8.5×10^{-8}	-0.017	—	—	—	1.3
			Effects on ϕ					
0.001	-0.021	$+0.075$	$+0.028$	-0.00045	—	—	—	0.08
0.01	-0.07	$+0.26$	$+3.5 \times 10^{-5}$	-0.00045	—	—	—	0.27
0.10	-0.05	$+0.28$	$+6.0 \times 10^{-6}$	-0.0040	—	—	—	0.28
1.00	-0.021	-0.15	$+1.0 \times 10^{-6}$	-0.0050	—	—	—	0.15
			Effects on L_ϕ					
0.001	-0.028	-2.4	-1.8×10^{-3}	-0.0056	$+2.1$	-6.6×10^{-4}	-0.011	3.2
0.01	-0.27	-1.5	-4.8×10^{-5}	-0.014	$+2.3$	-1.6×10^{-5}	-0.014	2.8
0.10	-0.44	-0.61	-3.5×10^{-6}	-0.027	$+2.3$	-1.1×10^{-6}	-0.018	2.4
1.00	-0.42	-0.22	-5.0×10^{-7}	-0.041	$+2.3$	-1.3×10^{-7}	-0.025	2.4

these species. However, using the "correspondence principle" of Criss and Cobble [83] and the parameters given by them in their table 1, the quantitiy (dC_p^o/dT) can be estimated for the aqueous species HSO_3^-, SO_3^{2-}, and $S_2O_5^{2-}$. Doing this, we obtain $(dC_p^o/dT) = +1.7$, -1.0, and $+1.5$ J mol^{-1} K^{-2} for HSO_3^-, SO_3^{2-}, and $S_2O_5^{2-}$, respectively. From data on the heat capacity of water and of $SO_2(g)$ [7,82], $(dC_p^o/dT) = +0.0066$ J mol^{-1} K^{-2} for $H_2O(l)$ and $(dC_p^o/dT) = +0.035$ J mol^{-1} K^{-2} for $SO_2(g)$; we estimate $(dC_p^o/dT) = 0$ for $SO_2^0(aq)$. These estimates are combined to yield values of $+1.7$, -2.7, -1.9, -0.035, and $+1.7$ J mol^{-1} K^{-2} for $(d\Delta C_p^o/dT)$ for processes (A), (B), (C), (D), and (E), respectively. These values are also given in table 9.

If eq (6) is used without including a $(d\Delta C_p^o/dT)$ term, values of $K_A = 0.00153$ mol kg^{-1} and $K_D = 0.213_3$ mol kg^{-1} bar^{-1} at 373.15 K are calculated. Inclusion of the $(d\Delta C_p^o/dT)$ terms and the estimates of them given above leads to $K_A = 0.00171$ mol kg^{-1} and $K_D = 0.212_8$ mol kg^{-1} bar^{-1} at 373.15 K. Thus, over the temperature range 273 to 373 K the thermodynamics of the $SO_2 + H_2O$ system are reasonably well described by the parameters given in tables 9 and 10. A plot of the measured Henry's Law constants as a function of temperature and the curve calculated using the final selected values given in table 9 are shown in figure 3. A particularly useful series of experiments would be the measurement of the heat capacities of aqueous sulfur dioxide solutions from 273 K to temperatures greater than 373 K.
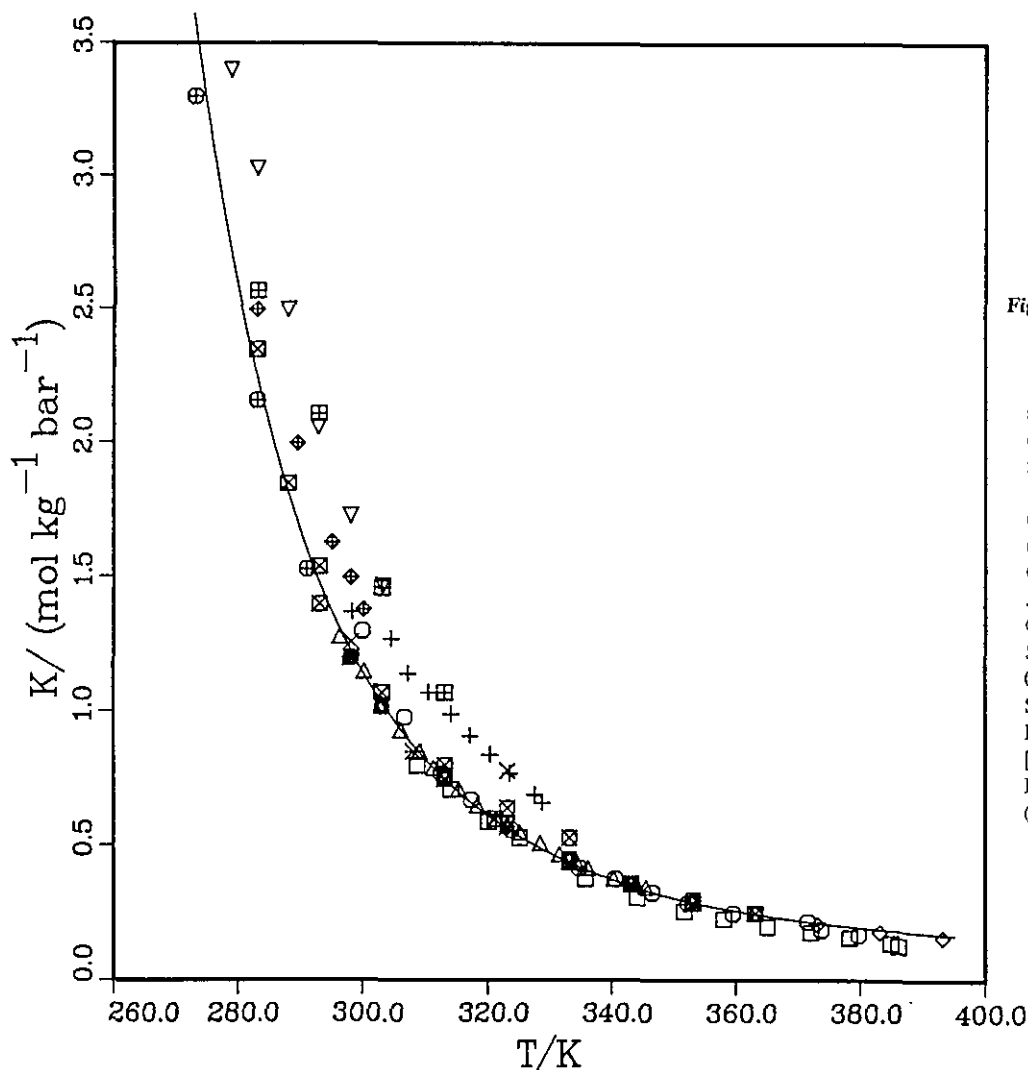
Figure 3-The measured Henry's Law constants as a function of temperature and the curve (solid line) calculated using the final selected values in table 9. The data sets and their corresponding symbols are: (⊠) Hudson [60]; (⬦) Maass and Maass [61]; (◇) Campbell and Maass [29]; (⊕) Morgan and Maass [31]; (⊡) Conrad and Beuschlein [58]; (×) Johnstone and Leppla [13]; (□, ○, △, and +) Beuschlein and Simenson [56] at, respectively, 0.51, 1.09, 4.36, and 7.45 g $SO_2/100$ g H_2O; (⊗) Rabe and Harris [62]; (⊗) Vosolobe et al. [64]; (⊞) Tokunaga [63]; (▽) Douabul and Reilly [59]; and (×) Byerley [57].

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Glossary

Roman

a	activity
f	fugacity
m	molality/mol kg^{-1}
n	amount or number of moles of substance
p	pressure
z	charge
A_m	Debye-Hückel constant; $A_m = 1.17642$ kg$^{1/2}$ mol$^{-1/2}$ at 298.15 K
B	parameter in Debye-Hückel equation
C_p	heat capacity at constant pressure
G	Gibbs energy
H	enthalpy
I	ionic strength
K	equilibrium constant
L_ϕ	relative apparent molar enthalpy, equal to H^{ex}/m
R	gas constant; $R = 8.31448$ J mol^{-1} K^{-1}
S	entropy
T	temperature

Greek

α	fraction
γ	activity coefficient
ϕ	osmotic coefficient
Δ	change

Superscripts

ex	excess
st	stoichiometric
o	value of a quantity which applies at the thermodynamic standard state
^{0}	designates a neutral species, i.e., SO_2^0
$^\wedge$	species quantity

Subscripts

f	formation property
ϕ	apparent molar quantity
$\pm$	mean ionic property
w	designates water

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