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The Second Dissociation Constant of Sulfuric Acid at Elevated Temperatures from Potentiometric Measurements

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Synopsis. The second dissociation constant of sulfuric acid in 1 *m* KCl media has been determined from 25 to 200 °C using Debye–Hückel equation from the data on the electromotive force of a hydrogen ion-concentration cell. The thermodynamic values for the $HSO_4^- = H^+ + SO_4^{2-}$ reaction and the KSO_4^- ion-pair association constant are also presented.

The sulfate ion plays an important role in the equilibrium,[1,2] rate,[3] and morphology[4] of the precipitation of inorganic compounds at elevated temperatures through complex formation with metal ions. However, the formation constants for sulfate complexes are very limited except for the hydrogensulfate ion.

Cobble and Criss[5–7] developed a method of estimating the equilibrium constant applicable up to the critical temperature using the entropy-corresponding principle. Recently, Helgeson[8] has proposed another method applicable to 600 °C and 5 kbar for geological applications. Such an estimation, however, can be applied only for simple single ions. Consequently, the formation constants for many complexes must be known to understand the effect of chemical species on the nature of reactions in solutions at elevated temperatures.

The second dissociation constant for sulfuric acid at elevated temperatures has been determined by solubility measurements[9,10] and conductivity measurements,[11,12] but not yet by emf measurements. A hydrogen ion-concentration cell at an elevated temperature was first used to determine the pH of the buffer solutions by Le Peintre et al.[13] Mesmer and Baes have since reviewed the hydrolysis of metal ions at a high ionic strength.[14] MacDonald has also investigated this reaction using the electrochemical method.[15] In the present study, we have determined the second dissociation constant of sulfuric acid at elevated temperatures by using potentiometric measurements as the first step to determine the formation constants of multivalent metal ions with sulfate ions.

Experimental

Materials. A stock solution of 0.1 mol dm^{-3} HCl was prepared from reagent-grade hydrochloric acid diluted with doubly distilled water. Reagent-grade KCl and K_2SO_4 were used without further purification. Ultrapure hydrogen (99.99999%) was used for the hydrogen electrode.

Hydrogen Ion-Concentration Cell.[16] The hydrogen ion-concentration cell consisted of a 300-cm^{-3} titanium autoclave containing a 180-cm^{-3} outer quartz beaker and an inner PTFE compartment, the two being joined by a liquid junction and each containing a platinized platinum hydrogen electrode. Figure 1 shows a cross-sectional view of the inner compartment. The porous PTFE disk (pore size, 0.2 μm; thickness, 1 mm) provides a liquid junction between the two compartments. The side of this compartment has a pin hole 0.7 mm in diameter which allows a rapid pressure-equilibration of hydrogen gas. Thus, the cell may be represented as:

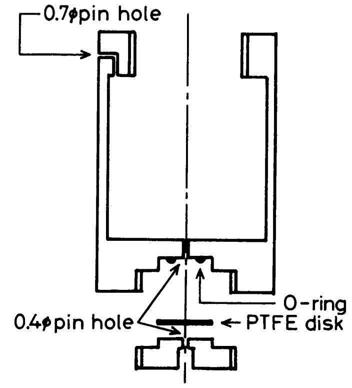

Fig. 1. Schematic of PTFE inner compartment.

$$\mathrm{Pt,H_2}\ \left|\begin{array}{l}\mathrm{HCl}(m_1)\\ \mathrm{K_2SO_4}(m_2)\\ \mathrm{KCl}(m_3=1)\end{array}\right\|\begin{array}{l}\mathrm{HCl}(m_4=0.001)\\ \mathrm{KCl}(m_5=1)\end{array}\left|\ \mathrm{H_2,Pt}\right. \qquad \text{(I)}$$

where *m* represents the molalities. The HCl concentration in the reference solution was 0.001 *m* in each experiment. The emf measurement was carried out for the 14 sets of composition as follows: m_1=0.0100—0.0240 and m_2= 0.0100—0.0250. In order to minimize the liquid junction potential and keep the ionic strength constant, KCl was added as a supporting electrolyte in both solutions (1 *m*). Because the PTFE is not wetted, the saturated KCl solution does not permeate the porous disk. We treated the disk using the following procedure: 1) wetting the porous disk with acetone and expelling air from the pores in the disk; 2) replacing the acetone with distilled water for a few days; 3) exchanging the water with a saturated KCl solution for two weeks. The cell was degassed after assembly by alternately pressurizing it with hydrogen and by venting it to atmospheric pressure several times. Finally, the cell was pressurized to about 0.5 MPa with hydrogen. The potential of the cell was measured over the temperature range from 25 to 200 °C at 25 °C intervals with a digital voltmeter. The voltage was recorded after a values had remained constant for several minutes ($\geqq \pm 1$ mV).

Results and Discussion

Since the pressure of hydrogen is equal in the two compartments, the potential of the cell (I) is given by Eq. 1:

$$E = (RT/F)\ln(a_{\mathrm{H^+,t}}/a_{\mathrm{H^+,r}}) + E_j \qquad (1)$$

where a_{H^+} is the activity of the hydrogen ion and where the subscripts t and r refer to the test solution and the reference solution respectively. E_j is the liquid junction potential, which can be estimated using the Henderson equation:[17]

$$E_j = -\Sigma D_i([i]_t - [i]_r) \qquad (2)$$

$$D_i = RT|Z_i|\lambda_i/(Z_i F\Sigma(|Z_i|[i]\lambda_i) \qquad (3)$$

where $[i]$ denotes the molality of the species i and λ_i is the limiting equivalent conductance of the i th ion. The values of λ_i are available over the above temperature range.[18]

The Debye-Hückel equation was used to calculate the activity coefficient:

$$\log\gamma_i = -Z_i^2 S\sqrt{I}/(1 + A\sqrt{I}) \qquad (4)$$

where S is the Debye-Hückel limiting slope, Z_i is the charge of the ionic species, and A is the adjustable parameter experimentally determined from the solubilities of various $M_m(SO_4)_n$ at elevated temperatures.[19,20] In the test solution, the major equilibrium reactions are as follows:

$$HSO_4^- \rightleftarrows H^+ + SO_4^{2-} \qquad (5)$$

$$K^+ + SO_4^{2-} \rightleftarrows KSO_4^- \qquad (6)$$

The equilibrium constants of the above reactions, expressed in logarithmic form, and combined with Eq. 4 are thus related to the concentrations and ionic strength respectively:

$$\log K_2 = \log([H^+][SO_4^{2-}]/[HSO_4^-]) - 4S\sqrt{I}/(1 + A\sqrt{I}) \qquad (7)$$

$$\log K_K = \log([KSO_4^-]/[K^+][SO_4^{2-}]) + 4S\sqrt{I}/(1 + A\sqrt{I}) \qquad (8)$$

The total analytical concentrations of H^+, SO_4^{2-}, and K^+ are expressed as $[H^+]+[HSO_4^-]=m_1$ (9), $[SO_4^{2-}]+[HSO_4^-]+[KSO_4^-]=m_2$ (10), and $[K^+]+[KSO_4^-]=2m_2+m_3$ (11). From Eqs. 7—11 we obtain the calculated concentration of $[H^+]_{cal}$ by the Newton-Raphson method. Combining $[H^+]_{cal}$ with Eq. 1 produces the calculated values of the potential at each temperature. Then we employed a computer program to analyze the equilibrium constants of sulfate complexes, i.e., the pair of K_2 and K_K which best account for all the observed potential data. The values obtained in this work are listed and compared with the literature values in Table 1, while they are illustrated in Fig. 2. Except for 298 K, the standard deviation between E_{obsd} and E_{calcd} increased with the increase in the temperature as follows: 298 K ±1.2%; 323 K ±0.6%; 348 K ±0.5%; 373 K ±0.6%; 398 K ±0.8; 423 K ±1.6%; 448 K ±2.3%; 473K ±3.1%.

Assuming that ΔC_p° varied as a quadratic function of the temperature, the values of log K_2 and log K_K obtained as functions of temperature were fitted by the least-squares method to give a five-parameter equation:

Table 1. Values of $\log K_2$ and $\log K_K$ as a Function of the Temperature

T/K	$-\log K_2$	$-\log K_2$[a]	$\log K_K$	$\log K_K$[b]
298	1.99	1.988	0.27	0.28
323	2.35	2.246	0.32	0.31
348	2.72	2.539	0.35	0.38
373	3.08	2.855	0.45	0.45
398	3.44	3.189	0.52	0.52
423	3.81	3.534	0.61	0.60
448	4.18	3.887	0.71	0.73
473	4.58	4.246	0.94	0.94

a) Marshall and Jones.[10] b) Calculated from Eq. 12.

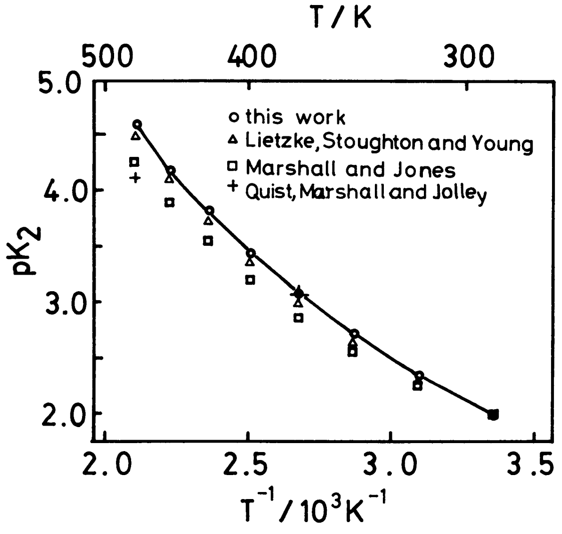

Fig. 2. pK_2 vs. T^{-1} for the second dissociation of sulfuric acid. Solid line is from Eq. 12.

$$\log K = a + b\log T + c/T + dT + eT^2 \qquad (12)$$

where T is the absolute temperature. For log K_2, the parameters a, b, c, d, and e are:

a=577.214, b=−246.01, c=−12717, d=0.283133, e=−1.37566×10^{-4} and for log K_k their values are:

a=−3072, b=1310.68, c=68881, d=−1.56182, e=7.1513×10^{-4}.

Usually, it is necessary to evaluate the A parameter as well as log K_2 to extrapolate the plots of log K_{app} vs. $\sqrt{I}/(1+A\sqrt{I})$ into an infinite dilution at each temperature. In the present study, however, the ionic strength in the test solution was fixed at 1 m in order that a liquid-junction potential should not exceed 1 mV. Thus, we used the literature value of the A parameter.[19,20] Nevertheless, the pK_2 values are substantially in agreement with the values determined by the solubility measurement at elevated temperatures[10] as well as with those reported by other investigators,[9–11] at 25 °C. In one earlier paper[10] the association of the calcium ion with sulfate was not assumed, but the existence of the $CaSO_4$ ion pair was pointed out later.[21] If the ion pair is present in the solution, it seems that the pK_2 values become higher,

Table 2. Thermodynamic Values for the $HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$ Reaction

T	$\Delta G°$	$\Delta H°$	$\Delta S°$	ΔC_p
K	kJ mol^{-1}	kJ mol^{-1}	J mol^{-1} K^{-1}	J mol^{-1} K^{-1}
298	11.4	−24.1	−119	−218
323	14.6	−29.2	−136	−192
348	18.1	−33.9	−149	−187
373	22.0	−38.7	−163	−200
398	26.3	−43.9	−176	−234
423	30.9	−50.6	−192	−287
448	35.9	−58.6	−211	−361
473	41.5	−68.6	−233	−452

as in the present work, than when without association.

The ion-pair association constant of KSO_4^- in the present study was somewhat lower than that determined by conductivity measurements.[22,23] There was some difficulty in obtaining a log K_K value for the present system. The log K values for the association of the univalent metal ion with the sulfate ion are considerably smaller than those of bi- and tervalent metal ions.[24] Thus, a weak complex of KSO_4^- results in a small contribution to the potential.

From the treatment of Eq. 12, the standard thermodynamic functions for changes in free energy ($\Delta G°$), enthalpy ($\Delta H°$), entropy ($\Delta S°$), and heat capacity ($\Delta C_p°$) were obtained for the temperature range from 25 to 200 °C. The values are given in Table 2. These values depend on the assumption of the dependency of $\Delta C_p°$ on the temperature. It is generally known that the standard heat capacities of ionic species in an aqueous solution show maximum values near 100 °C;[8] the $\Delta C_p°$ value in the present study indeed showed a maximum value at approximately 80 °C, in accordance with the maxima for $\Delta C_p°$ obtained for other ionization reactions.

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