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A Recalculation of the Dissociation Constants of $InSO_4^+$ and the Corresponding Thermodynamic Functions

AWADHESH MAHASETH†, S.K. JHA‡ and S.N. JHA*
Department of Chemistry
R.D. and D.J. College, Munger-811 201, India

We have recalculated the dissociation constants of $InSO_4^+$ at 5°, 15°, 25° and 35°C taking $In_2(SO_4)_{3T}$: H_2SO_{4T}: 4 : 5 using improved method of computation of results. From the knowledge of dissociation constants at different temperatures, the corresponding thermodynamic parameters have also been calculated.

INTRODUCTION

Hattox and Devries[1] measured the e.m.f. of the cells of the type

$$In(S) \mid In_2(SO_4)_3(m), Hg_2SO_4(m) \mid Hg \qquad (1)$$

where m lies between 0.00631 to 0.4233 at 5°, 15°, 25° and 35°C and calculated the activity coefficient pH, and freezing points of indium sulphate neglecting its hydrolysis.

Lietzke and Stoushton[2] studied the cell

$$In(S) \mid In_2(SO_4)_3 \,(M), Ag_2SO_4 \,(Sat) \mid Hg$$

using 0.01 to 2.3 M solution of indium sulphate at temperatures 15 to 70°C. They did not calculate the dissociation constants of $In(SO_4)_2^-$ or $InSO_4^+$. Sunden[3] measured, by e.m.f. method the thermodynamic dissociation constants of

(a) $InSO_4^+ \rightleftarrows In^{3+} + SO_4^{2-}$
(b) $In(SO_4)_2^- \rightleftarrows InSO_4^+ + SO_4^{2-}$
(c) $In(SO_4)_3^{3-} \rightleftarrows In(SO_4)_2^- + SO_4^{2-}$

at ionic strength equal to 2 at 20°C. He also neglected the hydrolysis of indium sulphate and used more concentrated solutions for which the activity coefficient equation used by us are not applicable. The values[4] of dissociation constants of $In(SO_4)_2^-$ and $InSO_4^+$ at 20°C and 2 ionic strength are 1.32×10^{-2} and 1.66×10^{-2} respectively. The formation of $In(SO_4)_3^{3-}$ and $InSO_4^+$ ions was supported by Sunden's anion exchange[5] measurements. He did not support the formation of $In(SO_4)_2^-$ ion. Nanda and Aditya[6] have also measured the thermodynamic dissociation constant of $InSO_4^+$ at 29–30°C by spectrophotometric method.

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†R.D.S.Y. Science College, Munger, T.M. Bhagalpur University, India.

‡Dr. J.M. College, Kathi Kund (Dumka) Sidho Kanhu University, Dumka, India.

EXPERIMENTAL

The dissociation constants of $InSO_4^+$ have been determined for a number of concentrations of indium sulphate and H_2SO_4 at 5°, 15°, 25° and 35°C from the study of the cell of the type

$$\begin{array}{c|ll|ll|lll|c} \mathrm{Pt} & \text{Q.H.}\ H_2SO_4 & (C_1) & H_2SO_4 & (C_1) & H_2SO_4 & (C_1) & Hg_2SO_4 & \mathrm{Hg} \\ & \text{Sat}\ In_2(SO_4)_3 & (C_2) & In_2(SO_4)_3 & (C_2) & In_2(SO_4)_3 & (C_2) & \text{Sat} & \end{array}$$

where Q.H. Stands for quinhydrone. Sulphuric acid (G.R.) and indium sulphate (Schuehardt Mon Cem) were used. Quinhydrone (A.R. Ranal Budapest) was purified using the method of Harned and wright[7]. The bridges used were similar to those suggest by Guggenheim[8]. For preparation of mercurous sulphate electrolytic method suggested by Hulett[9], was followed sulphuric acid solution was standarised by borex[10] using methyl red as indicator. In indium sulphate solution in dilute H_2SO_4, indium was estimated gravimetrically as oxinate[11] and total sulphate was quantitively estimated volumetrically; N_2 gas was used to remove dissolved oxygen from the experimental solution used in the cells. The temperature of the air thermostate was constant within ±0.05°C e.m.f. measurements were made with Tinsley vernier potentiometer and also with Bajaj vernier potentiometer using Bajaj mirror galvanometer. The e.m.f. values (absolute volt) given in Tables-1–4 are mean of the duplicate experiments of two cells (four experiments) which generally differed from one another by less than 0.10 mv. Stockholm convention has been followed for standard electrode potential.

RESULTS AND DISCUSSION

The e.m.f. of the cells (C-1) and (C-2)

$$\begin{array}{c|r|r|ll|ll} \mathrm{Pt} & \text{Q.H.}In_2(SO_4)(C_1) & In_2(SO_4)(C_1) & In_2(SO_4)_3(C_1) & \multirow{2}{*}{Hg_2SO_4} & \mathrm{Hg} & \text{(C-1)} \\ & H_2SO_4\ \ (C_2) & H_2SO_4\ \ (C_2) & H_2SO_4\ \ (C_2) & & & \end{array}$$

$$\mathrm{Pt}\ |\ \text{Q.H.}\ H_2SO_4\ \ (C)\ |\ H_2SO_4\ \ (C)\ |\ H_2SO_4\ \ (C)\ \ Hg_2SO_4\ |\ \mathrm{Hg} \qquad \text{(C-2)}$$

are given by the same equation:

$$E = E^0 - \frac{2.3026\,RT}{2\,F} \times \log\,[H^+]^2[SO_4^{2-}] + \frac{2.3026\,RT}{F} \times 3A\sqrt{\mu}$$
$$- \frac{2.3026\,RT}{2\,F} \times \beta\mu \qquad (1)$$

We have assumed that β does not depend on the composition of ionic atmosphere provided $\mu < 0.1$ and e.m.f. accuracy is ± 0.1 m.v. We have used the values of E^0 (molarity scale) and β reported by Sharma and Prasad[12].

Sharma and Prasad[12] equations corresponding to the dissociation constant of $HSO_4^- = H^+ + SO_4^{2-}$ and solubility product of Hg_2SO_4 are given below.

$$\log \frac{[H^+][SO_4^{2-}]}{[HgO_4^-]} = \log K + 4A\sqrt{\mu} - \beta\mu \qquad (2)$$

$$\log\,[Hg_2^{2+}][SO_4^{2-}] = \log K_{sp} + 8A\sqrt{\mu} - 2\beta\mu \qquad (3)$$

The values of constants used by us are the same as reported by Sharma and Prasad.[12]

H_2SO_4 dissociates according to the following Scheme:

$$\begin{array}{lcll} H_2SO_4 & \xrightarrow[\text{complete}]{\text{Ist step}} & H^+ \; + & HSO_4^- \\ & & C_2 & C_2(1-\alpha) \end{array}$$

$$\begin{array}{ll} H^+ \; + & SO_4^{2-} \\ C_2\alpha & C_2\alpha \end{array}$$

Hence for any mixture of $In_2(SO_4)_3$ and H_2SO_4, $[H^+] = (1+\alpha)C_2$, $[HSO_4^-] = (1-\alpha)C_2$, where α is the degree of dissociation of HSO_4^- and C_2 is the stoichiometric concentration of H_2SO_4. An arbitrary value is assigned to μ. The value of $[H^+]^2[SO_4^{2-}]$ is found from equation (1).

For the same ionic strength the value of $\dfrac{[H^+][SO_4^{2-}]}{[HSO_4^-]}$ is found from equation (2). Dividing the value of $[H^+]^2[SO_4^{2-}]$ by that of $\dfrac{[H^+][SO_4^{2-}]}{[HSO_4^-]}$, we get $[H^+][HSO_4^-]$ *i.e.* $(1-\alpha^2)C_2^2$, since C_2 is known, α may be calculated and hence $[H^+]$ and $[HSO_4^-]$ corresponding to the assumed value of μ are found.

The corresponding value of $[SO_4^{2-}]$ is calculated by dividing the value of $[H^+]^2[SO_4^{2-}]$ by that of $[H^+]^2$. Knowing the value of $[SO_4^{2-}]$, the corresponding value of $[Hg_2^{2+}]$ is calculated from equation (3). The corresponding values of $[In^{3+}]$, $[InSO_4^+]$ and $[In(SO_4)_2^-]$ are found from following equations:

$$[In]_T = [In^{3+}] + [InSO_4^+] + [In(SO_4)_2^-] \qquad (4)$$

on the conservation of matter and

$$3[In^{3+}] + [H^+] + [InSO_4^+] + 2[Hg_2^{2+}] + [In(SO_4)_2^-] + 2[SO_4^{2-}] + [HSO_4^-] \qquad (5)$$

based on electro-neutrality on adding equations (4) and (5) we get

$$2[In^{3+}] - 2[In(SO_4)_2^-] = 2[SO_4^{2-}] + [HSO_4^-] - [H^+] - [In]_T - 2[Hg_2^{2+}] \qquad (6)$$

Similarly multiplying equation (4) by three and adding to equation (5) we get

$$2[InSO_4^+] = 3[In]_T + [H^+] + 2[Hg_2^{2+}] - 2[SO_4^{2-}] - [HSO_4^-] - 4[In(SO_4)_2^-] \qquad (7)$$

on feeding the values of $[H^+][HSO_4^-]$, $[SO_4^{2-}]$, $[Hg_2^{2+}]$ and $[In]_T$ in equation (6) we get $2[In^{3+}] - 2[In(SO_4)_2^-]$. In a very dilute solution, if a preliminary assumption is made that $[In(SO_4)_2^-]$ ion is absent, we get the value of $[In^{3+}]$.

In case of these solutions, the value of $[InSO_4^+]$ is calculated from equation (7) assuming that $[In(SO_4)_2^-] = 0$. We get a new value of ionic strength from equation (8).

$$\mu = \frac{1}{2}[H^+] + \frac{1}{2}[HSO_4^-] + \frac{1}{2}[InSO_4^+] + 2[SO_4^{2-}] + 2[Hg_2^{2+}] + 4.5[In^{3+}] \qquad (8)$$

The process is repeated till μ becomes constant up to the 4th place of decimal.

TABLE-1

TEMPERATURE-5°C: DISSOCIATION $InSO_4^+ = In^{3+} + SO_4^{2-}$; $K_2(A) = [In^{3+}][SO_4^{2-}]/[InSO_4^+]$

$C_1 \times 10^4$	$C_2 \times 10^4$	E in abs m.v.	$[SO_4^{2-}] \times 10^4$	$[InSO_4^+] \times 10^4$	$[In^{3+}] \times 10^4$	$[In(SO_4)_2^-] \times 10^4$	$\mu \times 10^4$	$\log K_2(A) - \frac{12A\sqrt{\mu}}{1+\sqrt{\mu}}$
12. 18	15.24	133.16	29.40	17.16	3.29	3.89	109.47	–3.801
13.92	17.40	129.40	31.89	19.56	3.54	4.73	118.79	–3.819
15.66	19.58	126.01	34.60	21.46	4.15	5.70	130.04	–3.779
17.40	21.75	123.03	37.04	23.98	4.30	6.51	139.01	–3.800
19.15	23.94	120.16	40.64	25.16	5.82	7.31	155.34	–3.681
20.88	26.10	117.67	43.81	26.73	6.84	8.18	169.69	–3.631
22.62	28.28	115.41	46.35	28.75	7.32	9.16	180.32	–3.627

TABLE-2

TEMPERATURE-15°C: DISSOCIATION $InSO_4^+ = In^{3+} + SO_4^{2-}$

$C_1 \times 10^4$	$C_2 \times 10^4$	E in abs m.v.	$[SO_4^{2-}] \times 10^4$	$[InSO_4^+] \times 10^4$	$[In^{3+}] \times 10^4$	$[In(SO_4)_2^-] \times 10^4$	$\mu \times 10^4$	$\log K_2(A) - \frac{12A\sqrt{\mu}}{1+\sqrt{\mu}}$
15.66	19.58	134.08	33.41	23.29	2.94	5.09	124.02	–3.976
17.40	21.75	131.05	35.78	25.64	3.24	5.91	133.44	–3.966
19.15	23.94	128.27	38.17	27.89	3.63	6.77	143.29	–3.945
20.88	26.10	125.77	40.72	29.91	4.21	7.62	154.27	–3.905
22.62	28.28	123.46	43.17	31.96	4.75	8.52	164.92	–3.876

TABLE-3

TEMPERATURE-25°C: DISSOCIATION $InSO_4^+ = In^{3+} + SO_4^{2-}$

$C_1 \times 10^4$	$C_2 \times 10^4$	E in abs m.v.	$[SO_4^{2-}] \times 10^4$	$[InSO_4^+] \times 10^4$	$[In^{3+}] \times 10^4$	$[In(SO_4)_2^-] \times 10^4$	$\mu \times 10^4$	$\log K_2(A) - \frac{12A\sqrt{\mu}}{1+\sqrt{\mu}}$
10.44	13.05	154.14	27.17	15.55	3.16	2.16	103.37	–3.822
12.18	15.24	149.39	31.19	16.67	3.10	2.57	123.35	–3.631
13.92	17.40	145.43	34.51	18.30	6.46	3.06	137.59	–3.556
15.66	19.58	141.96	37.63	20.08	7.64	3.59	151.85	–3.514
17.40	21.75	138.85	41.06	21.49	9.18	4.11	168.28	–3.457
19.15	23.94	136.08	44.08	25.29	10.30	4.69	182.29	–3.437
20.88	26.10	133.66	46.15	25.07	12.57	5.69	191.40	–3.379
22.62	28.28	131.41	47.85	28.69	10.37	6.17	197.39	–3.515

TABLE-4

TEMPERATURE-35°C: DISSOCIATION $InSO_4^+ \rightleftharpoons In^{3+} + SO_4^{2-}$

$C_1 \times 10^4$	$C_2 \times 10^4$	E in abs m.v.	$[SO_4^{2-}] \times 10^4$	$[InSO_4^+] \times 10^4$	$[In^{3+}] \times 10^4$	$[In(SO_4)_2^-] \times 10^4$	$\mu \times 10^4$	$\log K_2(A) - \frac{12A\sqrt{\mu}}{1+\sqrt{\mu}}$
12.18	15.24	156.79	37.12	9.75	1.23	2.28	163.37	–4.035
13.92	17.40	152.82	42.09	9.69	1.56	2.52	189.55	–3.923
15.66	19.58	149.36	46.59	10.03	1.84	2.85	213.07	–3.865
17.40	21.75	145.30	51.04	10.37	2.12	3.18	236.55	–3.812
19.15	23.94	143.56	55.64	10.56	2.42	3.49	261.25	–3.761
20.88	26.10	141.09	60.34	10.59	2.74	3.75	286.68	–3.710

When we increased the concentration beyond a certain limit, we found that $[In^{3+}]$ was almost zero. Hence, it was decided to take concentrations slightly above this range and assume that $[In^{3+}] = 0$.

At such high concentration, values of $[H^+]$, $[HSO_4^-]$, $[SO_4^{2-}]$ and $[Hg_2^{2+}]$ for an arbitrary value of μ are determined as described earlier. These values of concentrations for the various ionic species are put in equation (6) and it is assumed that $[In^{3+}] = 0$. So we get a value of $[In(SO_4)_2^-]$. By feeding all these values in equation (7). we get a value of $[InSO_4^+]$. A new value of ionic strength is found from equation (9).

$$\mu = \frac{1}{2}[H^+] + \frac{1}{2}[HSO_4^-] + \frac{1}{2}[InSO_4^+] + \frac{1}{2}[In(SO_4)_2^-] + 2[SO_4^{2-}] + 2[Hg_2^{2+}] \quad (9)$$

This process is repeated till μ becomes constant up to fifth place of decimal. The concentrations of ionic species at this stage are assumed to be exact concentrations. Now, thermodynamic dissociation constant of $In(SO_4)_2^-$

$$K_1 = \frac{{}^{a}InSO_4^+ \, {}^{a}SO_4^{2-}}{{}^{a}In(SO_4)_2^-} \quad (10)$$

Equation (10) can be written as follows:

$$\log \frac{[InSO_4^+][SO_4^{2-}]}{[In(SO_4)_2^-]} - \frac{4A\sqrt{\mu}}{1+\sqrt{\mu}} = \log K_1 - b\mu \quad (11)$$

Taking a number of solutions with different ionic strengths and plotting L.H.S. of equation (11) against μ , we get linear plots at all the four temperatures. The values of K_1 and μ have been calculated from these plots at different temperatures and have been reported earlier. The corresponding thermodynamic functions have also been calculated.

In more dilute solution of $In_2(SO_4)_3$ in H_2SO_4, the total indium is present as In^{3+}, $InSO_4^+$ and $In(SO_4)_2^-$ ions. By the process outlined, below the value of $In(SO_4)_2^-$ need not be neglected while calculating $[In^{3+}]$ as done by Sharma and Prasad[12].

At lower concentrations the value of $[H^+]$, $[HSO_4^-]$, $[SO_4^{2-}]$ and $[Hg_2^{2+}]$ corresponding to an arbitrary value of μ are calculated as done earlier. Now the values of $[SO_4^{2-}]$, K_1 and b are put in equation (11), when we get a ratio of $[InSO_4^+]$ to $[In(SO_4)_2^-]$. The values of $[In^{3+}]$, $[InSO_4^+]$ and $[In(SO_4)_2^-]$ can be found out with the help of equations (6), (7) and (12)

$$\frac{[InSO_4^+]}{[In(SO_4)_2^-]} = K^1 \quad (12)$$

where K^1 is a known quantity. A new value of μ is now calculated from

$$\mu = \frac{1}{2}[H^+] + \frac{1}{2}[HSO_4^-] + \frac{1}{2}[InSO_4^+] + \frac{1}{2}[In(SO_4)_2^-] + 2[Hg_2^{2+}] + 2[SO_4^{2-}] + 4.5[In^{3+}] \quad (13)$$

The whole process is repeated till the ionic strength is constant upto the sixth place of decimal. The ionic concentrations at this stage are assumed to be correct. Now thermodynamic dissociation constant of $InSO_4^+$ *i.e.*,

$$K_2 = \frac{{}^{a}In^{3+} \cdot {}^{a}SO_4^{2-}}{{}^{a}InSO_4^+}$$

$$\frac{[In^{3+}][SO_4^{2-}]}{[InSO_4^{4+}]} \times \frac{{}^{f}In^{3+} \cdot {}^{f}SO_4^{2-}}{{}^{f}InSO_4^+} \quad (14)$$

Equation (14) reduces itself to

$$\log \frac{[In^{3+}][SO_4^{2-}]}{[InSO_4^+]} - \frac{12A\sqrt{\mu}}{1+\sqrt{\mu}} = \log K_2 - B_1\mu \quad (15)$$

where $B_1 = {}^{B}In^{3+} + {}^{B}SO_4^{2-} - {}^{B}InSO_4^+$

Taking a number of solutions of different ionic strengths and plotting L.H.S. of equation (15) against μ, we get linear plots at all the four temperatures.

The experimental results are given in Tables 1–4. The values of K_2 at different temperatures are given in Table-5.

TABLE-5

Temp. (°C)	5		15		25		35	
	Our values	Jha and Prasad's values	Our values	Jha and Prasad's values	Our values	Jha and Prasad's values	Our values	Jha and Prasad's values
$K_2 \times 10^5$	5.75	4.27	4.57	6.53	9.62	21.38	4.37	53.09

A plot of log K_2 against $\frac{1}{T}$ is linear. The value of ΔH has been found from the slope of this plot. The values of ΔG and ΔS have been found from well known equations. These values are given in Table-6.

TABLE-6

Temp. (°C)	5	15	25	35
ΔH in cals	4888	5195	5130	5584
ΔG in cals	5397	5724	5676	6108
–ΔS in eu	1.83	1.80	1.83	1.70

The values of thermodynamic parameters are presented in Table-6. Out values of K_2 are of the same order as that of[13] $AlSO_4^+ \rightleftarrows Al^{3+} + SO_4^{2-}$ and of[14] $CrSO_4^+ \rightleftarrows Cr^{3+} + SO_4^{2-}$ and of[14] $InSO_4^+ \rightleftarrows In^{3+} + SO_4^{2-}$.

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