

## Ionic Equilibria in Tri-Bivalent Salts (Indium Alum) at 15°C.

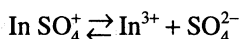
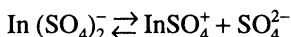
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We have measured the dissociation constants of  $\text{In}(\text{SO}_4)_2^-$  and  $\text{InSO}_4^+$  at 15°C by E.M.F. method taking  $[\text{In}_2(\text{SO}_4)_3]_{\text{T}} : [\text{H}_2\text{SO}_4]_{\text{T}} : 1 : 1$ . Our values are of the same order as those of Jha and Prasad, who had taken  $[\text{In}_2(\text{SO}_4)_3]_{\text{T}} : [\text{H}_2\text{SO}_4]_{\text{T}} : 4 : 5$ . The method of computation of result has been improved.

### INTRODUCTION

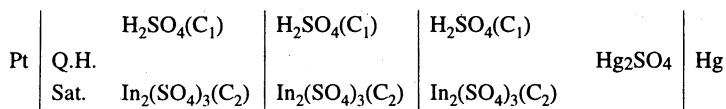
A large number of workers have studied the dissociation constants of the salt indium sulphate using different methods<sup>1-6</sup>. Jha and Prasad<sup>7</sup> have also measured the thermodynamic dissociation constants (by e.m.f. method) of



at 5°, 15°, 25° and 35°C taking indium sulphate and  $\text{H}_2\text{SO}_4$  in the molar ratio 4 : 5. In the present work, we have taken  $[\text{In}_2(\text{SO}_4)_3]_{\text{T}} : [\text{H}_2\text{SO}_4]_{\text{T}} : 1 : 1$  and calculated thermodynamic dissociation constants of  $\text{In}(\text{SO}_4)_2^- \rightleftharpoons \text{InSO}_4^+ + \text{SO}_4^{2-}$  and  $\text{InSO}_4^+ \rightleftharpoons \text{In}^{3+} + \text{SO}_4^{2-}$  at 15°C only. Our values of dissociation constants are of the same order as those reported by Jha and Prasad<sup>7</sup>.

### EXPERIMENTAL

The dissociation constants of  $\text{In}(\text{SO}_4)_2^-$  and  $\text{InSO}_4^+$  have been determined at 15°C from the study of the cells of the type



where Q.H. stands for quinhydrone.  $\text{In}_2(\text{SO}_4)_3$  and  $\text{H}_2\text{SO}_4$  were mixed in the ratio 1 : 1 and the cell was studied at 15°C for a number of concentrations of  $\text{In}_2(\text{SO}_4)_3$  and  $\text{H}_2\text{SO}_4$ . Sulphuric acid (G.R. sample) and indium sulphate (Schuchardt Noncem) were used Quinhydrone of analytical grade (Ranalbuda

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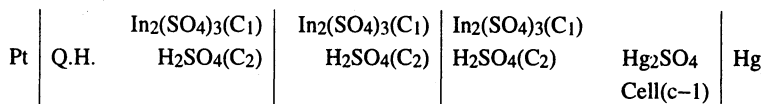
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Pest) was crystallised and dried before used, following the method of Harned and Wright<sup>8</sup>. The bridges were of the type suggested by Guggenheim<sup>9</sup> with slight modification.

The mercurous sulphate was prepared by electrolytic method devised by Hulett<sup>10</sup>. Stock solution of sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) was prepared and standardised against lorex<sup>11</sup>. Stock solution of indium sulphate [In<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>] in dilute sulphuric acid was prepared and indium was estimated gravimetrically as oxinate<sup>12</sup>. In order to know the total amount of sulphate in the stock solution, a definite quantity of stock solution of In<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> in dilute sulphuric acid was boiled with a known volume of standard Na<sub>2</sub>CO<sub>3</sub> solution for about an hour, cooled and the excess of Na<sub>2</sub>CO<sub>3</sub> was titrated with standard H<sub>2</sub>SO<sub>4</sub> solution. All solutions were prepared at the experimental temperature, Presaturated nitrogen gas was used to remove oxygen from the solution used in the cells. The temperature of air thermostat was constant within  $\pm 0.05^\circ\text{C}$ . E.M.F. measurements were made with a Tinsley vernier potentiometer Type 4363 make 1942 (Tinsley and Co. Ltd., Werdsee Hall) using a Bajaj mirror Galvanometer, Type M.G.8 (Sensitivity  $3.92 \times 10^{-10}$  amps/m.m.). The e.m.f. values (absolute volt) given in Table 1 and 2 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 potentials.

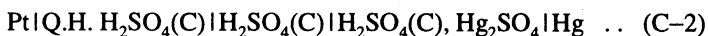
## RESULTS AND DISCUSSION

We have measured the dissociation constants of  $\text{In}(\text{SO}_4)_2^- \rightleftharpoons \text{InSO}_4^+ + \text{SO}_4^{2-}$  and  $\text{InSO}_4^+ \rightleftharpoons \text{In}^{3+} + \text{SO}_4^{2-}$  using cells of the type



where Q.H. stands for quinhydrone. With our experimental values of e.m.f. (Stockholm convention) and stoichiometric concentration of In<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> the values of the dissociation constants have been calculated at 15°C. All concentration terms are in mol dm<sup>-3</sup>.

The e.m.f. of cells (C-1) and (C-2) are given in equation (1).



$$E = E^\circ - \frac{2.3026RT}{2F} \log [\text{H}^+]^2 [\text{SO}_4^{2-}] + \frac{2.3026RT}{F} \times 3A\sqrt{\mu} - \frac{2.3026RT}{2F} \beta\mu \quad (1)$$

The values of  $E^\circ$  (-0.0857 abs. volt molarity scale) and  $\beta$ (3.99) were found from the cell given in this paragraph<sup>13</sup>. Sharma and Prasad's equation<sup>14, 15</sup> corresponding to the dissociation.

$\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}$  and solubility product of Hg<sub>2</sub>SO<sub>4</sub> both at 15°C are given below.

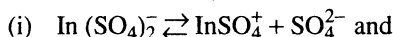
$$\log \frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = \bar{2}.200 + 2.0008\sqrt{\mu} - 3.41176\mu \quad (2)$$

where  $\log K = \bar{2}.200$

$$\text{and} \quad \log [\text{Hg}_2^{2+}][\text{SO}_4^{2-}] = \bar{7}.87040 + 4.0016\sqrt{\mu} - 6.82352\mu \quad (3)$$

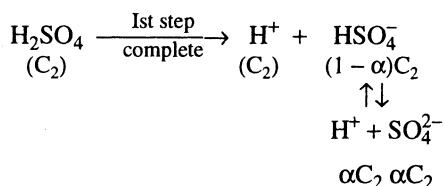
where  $\log K_{sp} = \bar{7}.87040$

The data concerning the dissociation of



(ii)  $\text{InSO}_4^+ \rightleftharpoons \text{In}^{3+} + \text{SO}_4^{2-}$  are given in Tables 1 and 2 respectively.

$\text{H}_2\text{SO}_4$  dissociates according to the following scheme



Hence for any mixture of  $\text{In}_2(\text{SO}_4)_3$  and  $\text{H}_2\text{SO}_4$ ;  $[\text{H}^+] = (1 + \alpha)\text{C}_2$ ,  $[\text{HSO}_4^-] = (1 - \alpha)\text{C}_2$  where  $\alpha$  is the degree of dissociation of  $\text{HSO}_4^-$  and  $\text{C}_2$  is the stoichiometric concentration of  $\text{H}_2\text{SO}_4$ . A rough value is assigned to  $\mu$ . The value of  $[\text{H}^+]^2[\text{SO}_4^{2-}]$  is found from equation (1). For the same ionic strength the value of  $[\text{H}^+][\text{SO}_4^{2-}] / [\text{HSO}_4^-]$  is found from equation (2). Dividing the value of  $[\text{H}^+]^2[\text{SO}_4^{2-}]$  by that of  $[\text{H}^+][\text{SO}_4^{2-}] / [\text{HSO}_4^-]$ , we get  $[\text{H}^+][\text{HSO}_4^-]$  i.e.,  $(1 - \alpha^2)\text{C}_2^2$ . Since  $\text{C}_2$  is known,  $\alpha$  may be calculated and hence  $[\text{H}^+]$  and  $[\text{HSO}_4^-]$  corresponding to the assumed of  $\mu$  are found out. The corresponding value of  $[\text{SO}_4^{2-}]$  is calculated by dividing the value of  $[\text{H}^+]^2[\text{SO}_4^{2-}]$  by that of  $[\text{H}^+]^2$ . Knowing the value of  $[\text{SO}_4^{2-}]$ , the corresponding value of  $[\text{Hg}_2^{2+}]$  is calculated from equation (3). The corresponding values of  $[\text{In}^{3+}]$ ,  $[\text{InSO}_4^+]$ , and  $[\text{In}(\text{SO}_4)_2]$  are found out from following equation

$$[\text{In}]_T = [\text{In}^{3+}] + [\text{InSO}_4^+] + [\text{In}(\text{SO}_4)_2] \quad (4)$$

based on the conservation of matter and

$$3[\text{In}^{3+}] + [\text{H}^+] + [\text{InSO}_4^+] + 2[\text{Hg}_2^{2+}] = [\text{In}(\text{SO}_4)_2] + 2[\text{SO}_4^{2-}] + [\text{HSO}_4^-] \quad (5)$$

based on electroneutrality.

On adding equations (4) and (5), we get

$$2[\text{In}^{3+}] - 2[\text{In}(\text{SO}_4)_2] = 2[\text{SO}_4^{2-}] + [\text{HSO}_4^-] - [\text{H}^+] - [\text{In}]_T - 2[\text{Hg}_2^{2+}] \quad (6)$$

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

$$2[\text{InSO}_4^+] = 3[\text{In}]_T + [\text{H}^+] + 2[\text{Hg}_2^{2+}] - 2[\text{SO}_4^{2-}] - [\text{HSO}_4^-] - 4[\text{In}(\text{SO}_4)_2] \quad (7)$$

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 very dilute solution, if a preliminary assumption is made that  $In(SO_4)_2^-$  ion is absent, we get 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 the equation

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

This process is repeated till  $\mu$  becomes constant up to 4th place of decimal. When we increased the concentrations beyond a certain limit, we found that  $[In^{3+}]$  was almost zero. Hence it was decided to take concentration 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  $\mu$  are determined as described earlier. These values 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 ( $\mu$ ) is found from the equation

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

This process is repeated till  $\mu$  becomes constant upto four or five in the fifth place of decimal. The concentrations of the ionic species at this stage are assumed

TABLE-1  
TEMPERATURE  $15^\circ C \pm 0.05^\circ C$ ; DISSOCIATION:  $In(SO_4)_2^- \rightleftharpoons InSO_4^+ + SO_4^{2-}$

$C_1 \times 10^4$	$C_2 \times 10^4$	E in abs. m.V.	$[SO_4^{2-}]$ $\times 10^4$	$[InSO_4^+]$ $\times 10^4$	$[In(SO_4)_2^-]$ $\times 10^4$	$\mu \times 10^4$	$\log K_1(A) = \frac{4A\sqrt{\mu}}{1 + \sqrt{\mu}}$
35.06	35.06	117.56	46.79	53.67	16.44	171.8	-2.048
42.08	42.08	112.47	52.46	62.85	21.31	196.6	-2.056
49.09	49.09	108.28	57.28	71.18	27.00	219.9	-2.079
63.12	63.12	101.32	68.26	90.26	35.98	268.8	-2.048
70.12	70.12	98.48	72.87	98.91	41.28	292.2	-2.049

to be the exact concentrations and they are given Table 1. Now, thermodynamic dissociation constant of  $In(SO_4)_2^-$

$$K_1 = \frac{a_{InSO_4^+} \cdot a_{SO_4^{2-}}}{a_{In(SO_4)_2^-}}$$

$$= \frac{[InSO_4^+][SO_4^{2-}]}{[In(SO_4)_2^-]} \times \frac{f_{InSO_4^+} \cdot f_{SO_4^{2-}}}{f_{In(SO_4)_2^-}} \dots \quad (8)$$

Equation (8) can be written as follows

$$\log \frac{[\text{InSO}_4^+][\text{SO}_4^{2-}]}{[\text{In}(\text{SO}_4)_2^-]} - \frac{4A\sqrt{\mu}}{1 + \sqrt{\mu}} = \log K_1 - b\mu \dots \quad (9)$$

where  $b = {}^b\text{InSO}_4^+ + {}^b\text{SO}_4^{2-} - {}^b\text{In}(\text{SO}_4)_2^-$

Taking a number of solutions with different ionic strengths (Table 1) and plotting L.H.S. of equation (9) against  $\mu$ , we get a straight line. The straight line is drawn in such a manner that equal and least number of squares lie above and below the straight line. We get the values of  $K_1$  and  $b$  from the plot. In this way the values of  $K_1$  and  $b$  have been calculated at 15°C.

In more dilute solution of  $\text{In}_2(\text{SO}_4)_3$  in  $\text{H}_2\text{SO}_4$ , the total indium is present as  $\text{In}^{3+}$ ,  $\text{InSO}_4^+$  and  $\text{In}(\text{SO}_4)_2^-$  ions. By the process outlined below, the value of  $[\text{In}(\text{SO}_4)_2^-]$  need not be neglected while calculating  $[\text{In}^{3+}]$  as done by Sharma and Prasad<sup>16</sup>.

At lower concentrations the values of  $[\text{H}^+]$ ,  $[\text{HSO}_4^-]$ ,  $[\text{SO}_4^{2-}]$  and  $[\text{Hg}_2^{2+}]$  corresponding to a rough value of  $\mu$  are calculated as done earlier. Now the values of  $[\text{SO}_4^{2-}]$ ,  $K_1$  and  $b$  are put in equation (9), when we get a ratio of  $[\text{InSO}_4^+]$  to  $[\text{In}(\text{SO}_4)_2^-]$ . The values of  $[\text{In}^{3+}]$ ,  $[\text{InSO}_4^+]$  and  $[\text{In}(\text{SO}_4)_2^-]$  can be found out with the help of equations (6), (7) and (10) *i.e.*

$$\frac{[\text{InSO}_4^+]}{[\text{In}(\text{SO}_4)_2^-]} = K^1 \quad (10)$$

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

$$\mu = \frac{1}{2}[\text{H}^+] + \frac{1}{2}[\text{HSO}_4^-] + \frac{1}{2}[\text{InSO}_4^+] + \frac{1}{2}[\text{In}(\text{SO}_4)_2^-] + 2[\text{SO}_4^{2-}] + 2[\text{Hg}_2^{2+}] + 4.5[\text{In}^{3+}]$$

The whole process is repeated till the ionic strength becomes constant up to four or five in the sixth place of decimal. The ionic concentrations at this stage are assumed to be correct and are given in Table 2.

TABLE 2  
TEMPERATURE 15°C ± 0.05°C; DISSOCIATION  $\text{InSO}_4^+ \rightleftharpoons \text{In}^{3+} + \text{SO}_4^{2-}$

$C_1 \times 10^4$	$C_2 \times 10^4$	E abs. m.V.	$[\text{SO}_4^{2-}]$ $\times 10^4$	$[\text{InSO}_4^+]$ $\times 10^4$	$[\text{In}^{3+}]$ $\times 10^4$	$[\text{In}(\text{SO}_4)_2^-]$ $\times 10^4$	$\mu \times 10^4$	$\log K_2(A) - \frac{12A\sqrt{\mu}}{1 + \sqrt{\mu}}$
12.03	12.03	147.95	25.54	19.15	1.35	3.56	92.73	-4.271
14.03	14.03	143.56	27.58	22.48	1.10	4.48	99.38	-4.408
16.02	16.02	139.76	29.68	25.49	1.16	5.40	106.97	-4.434
18.02	18.02	136.15	33.45	26.83	2.96	6.25	125.01	-4.079
20.06	20.06	133.05	35.84	29.54	3.29	7.30	134.69	-4.023

Now thermodynamic dissociation constant of  $\text{InSO}_4^+$  *i.e.*

$$K_2 = \frac{{}^a\text{In}^{3+} \cdot {}^a\text{SO}_4^{2-}}{{}^a\text{InSO}_4^+}$$

$$= \frac{[\text{In}^{3+}][\text{SO}_4^{2-}]}{[\text{InSO}_4^+]} \times \frac{f_{\text{In}^{3+}} \cdot f_{\text{SO}_4^{2-}}}{f_{\text{InSO}_4^+}} \quad (11)$$

Equation (11) reduces itself to

$$\log \frac{[\text{In}^{3+}][\text{SO}_4^{2-}]}{[\text{InSO}_4^+]} - \frac{12A\sqrt{\mu}}{1 + \sqrt{\mu}} = \log K_2 - B\mu \quad (12)$$

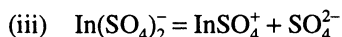
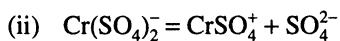
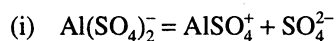
where  $B = {}^B\text{In}^{3+} + {}^B\text{SO}_4^{2-} - {}^B\text{InSO}_4^+$

Taking a number of solutions of different ionic strengths (Table 2) and plotting the L.H.S. of equation (12) against  $\mu$ , a straight line is obtained. The values of  $K_2$  and  $B$  are found from plot.

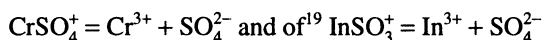
The thermodynamic dissociation constants at 15°C, thus found are given below

	Value	Dissociation
$K_1$	$9.55 \times 10^{-3}$	$\text{In}(\text{SO}_4)_2^- = \text{InSO}_4^+ + \text{SO}_4^{2-}$
$K_2$	$3.47 \times 10^{-6}$	$\text{InSO}_4^+ = \text{In}^{3+} + \text{SO}_4^{2-}$

Our values of  $K_1$  is of the same order as that<sup>17-19</sup> of



Similarly our values of  $K_2$  is of the same order as of<sup>18</sup>



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