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# A Recalculation of the Dissociation Constant of $AlSO_4^+$ and the Corresponding Thermodynamic Functions

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We have measured the dissociation constant of $AlSO_4^+ \rightleftarrows Al^{3+} + SO_4^{2-}$ at 5°, 15°, 25° and 35°C from Sharma and Prasad's values of EMF of Cell-$C_1$ and other data using improved equations and modifying the method of computation of results. Our results are entirely different from those reported by Sharma and Prasad.

## INTRODUCTION

The dissociation constants of $Al(SO_4)_2^- = AlSO_4^+ + SO_4^{2-}$ and $AlSO_4^+ = Al^{3+} + SO_4^{2-}$ were measured by Sharma and Prasad[1], using cell (C–1).

$$\mathrm{Pt}\left|\ \mathrm{Q.H.}\ \begin{array}{ll}\mathrm{Al_2(SO_4)_3} & (C_1)\\ \mathrm{H_2SO_4} & (C_2)\end{array}\right|\begin{array}{ll}\mathrm{Al_2(SO_4)_3} & (C_1)\\ \mathrm{H_2SO_4} & (C_2)\end{array}\left|\begin{array}{ll}\mathrm{Al_2(SO_4)_3} & (C_1)\,\mathrm{Hg_2SO_4}\\ \mathrm{H_2SO_4} & (C_2)\end{array}\right|\mathrm{Hg}\quad (C\text{–}1)$$

Q.H. = quinhydrone

However, they did not take into acount the $Hg_2^{2+}$ ion. Jha and Jha[2] had revised their results at 35°C only taking into account the concentration of $Hg_2^{2+}$ ion, but their method of plotting was inaccurate.

In the present work Sharma and Prasad's experimental data for mixtures of $Al_2(SO_4)_3$ and $H_2SO_4$ have been used[1] to recalculate the values of dissociation constants of $AlSO_4^+ = Al^{3+} + SO_4^{2-}$ at 5°, 15°, 25° and 35°C after taking into consideration the concentration of mercurous ion and modifying the method of plotting.

All concentration terms are in mole/litre. Concentrations are indicated by [ ].

## RESULTS AND DISCUSSION

The E.M.F. of the cells (C–1)

$$\mathrm{Pt}\left|\ \mathrm{Q.H.}\ \begin{array}{ll}\mathrm{Al_2(SO_4)_3} & (C_1)\\ \mathrm{H_2SO_4} & (C_2)\end{array}\right|\begin{array}{ll}\mathrm{Al_2(SO_4)_3} & (C_1)\\ \mathrm{H_2SO_4} & (C_2)\end{array}\left|\begin{array}{ll}\mathrm{Al_2(SO_4)_3} & (C_1)\,\mathrm{Hg_2SO_4}\\ \mathrm{H_2SO_4} & (C_2)\end{array}\right|\mathrm{Hg}\quad (C\text{–}1)$$

and the E.M.F of the cells (C–2),

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

are given by the same equation:

$$E = E^\circ - \frac{2.3026RT}{2F} \times \log [H^+]^2[SO_4^{2-}] + \frac{2.3026\ RT}{F} \times 3A\sqrt{\mu}$$

$$- \frac{2.3026RT}{2F} \times \beta\mu \tag{1}$$

The values of E° (molarity scale) and β were reported by Sharma and Prasad[3]. Sharma and Prasad's equations[4,5] corresponding to the dissociation constant of $HSO_4^- = H^+ + SO_4^{2-}$ and solubility product of $Hg_2SO_4$ are given below:

$$\log \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} = \log K + 4A\sqrt{\mu} - B\mu \tag{2}$$

$$\log [Hg_2^{2+}][SO_4^{2-}] = \log K_{sp} + 8A\sqrt{\mu} - 2B\mu \tag{3}$$

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

$H_2SO_4$ dissociates according to the following scheme:

$$\begin{array}{lcl}
H_2SO_4 & \xrightarrow[\text{Complete}]{\text{1st Step}} & H^+ \ + \ HSO_4^- \\
C_2 & & C_2 \quad C_1(1-\alpha) \\
 & & \qquad \downarrow\uparrow \\
 & & H^+ \ + \ SO_4^{2-} \\
 & & C_2\alpha \quad C_2\alpha
\end{array}$$

Hence for any mixture of $Al_2(SO_4)_3$ 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 $[H^+][SO_4^{2-}]/[HSO_4^-]$ is found from equation (2). Dividing the value of $[H^+]^2[SO_4^{2-}]$ by that of $\frac{[H^+][SO_4^{2-}]}{[HSO_4^-]}$, 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 value of $[Al^{3+}]$, $[AlSO_4^+]$ and $[Al(SO_4)_2^-]$ are found from following equations:

$$[Al]_T = [Al^{3+}] + [AlSO_4^+] + [Al(SO_4)_2^-] \tag{4}$$

based on the conservation of matter and

$$3[Al^{3+}] + [H^+] + [AlSO_4^+] + 2[Hg_2^{2+}] = [Al(SO_4)_2^-] + 2[SO_4^{2-}] + [HSO_4^-] \qquad (5)$$

based on electro-neutrality.

Sharma and Prasad had used the equation:

$$3[Al^{3+}] + [H^+] + [AlSO_4^+] = [Al(SO_4)_2^-] + 2[SO_4^{2-}] + [HSO_4^-] \qquad (6)$$

instead of equation (5). Since the ionic concentration of $Hg_2^{2+}$ ion is of the same order as that of $Al(SO_4)_2^-$ ion, the concentration of former ion cannot be neglected. On adding equations (4) and (5), we get

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

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

$$2[AlSO_4^+] = 3[Al]_T + [H^+] + 2[Hg_2^{2+}] - 2[SO_4^{2-}] - [HSO_4^-] - 4[Al(SO_4)_2^-] \qquad (8)$$

On feeding the values of $[H^+]$, $[HSO_4^-]$, $[SO_4^{2-}]$, $[Hg_2^{2+}]$ and $[Al]_T$ in equation (7), we get $2[Al^{3+}] - 2[Al(SO_4)_2^-]$. In a very dilute solution, if a preliminary assumption is made that $[Al(SO_4)_2^-]$ ion is absent, we get the value of $[Al^{3+}]$.

In case of these solutions, the value of $[AlSO_4^+]$ is calculated from equation (8) assuming that $[Al(SO_4)_2^-] = 0$. We get a new value of ionic strength from equation (9).

$$\mu = \tfrac{1}{2}[H^+] + \tfrac{1}{2}[HSO_4^-] + \tfrac{1}{2}[AlSO_4^+] + 2[SO_4^{2-}] + 2[Hg_2^{2+}] + 4.5[Al^{3+}] \qquad (9)$$

The process is repeated till μ becomes constant upto the 4th place of decimal. When we increased the concentrations beyond a certain limit, we found that $[Al^{3+}]$ was almost zero. Hence, it was decided to take concentrations slightly above this range and assume that $[Al^{3+}] \approx 0$.

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 (7) and it is assumed that $[Al^{3+}] = 0$. So we get a value of $[Al(SO_4)_2^-]$. By feeding all these values in equation (8), we get a value of $[AlSO_4^+]$. A new value of ionic strength is found from equation (10).

$$\mu = \tfrac{1}{2}[H^+] + \tfrac{1}{2}[HSO_4^-] + \tfrac{1}{2}[AlSO_4^+] + \tfrac{1}{2}[Al(SO_4)_2^-] + 2[SO_4^{2-}] + 2[Hg_2^{2+}] \qquad (10)$$

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 $Al(SO_4)_2^-$

$$K_1 = \frac{a_{AlSO_4^+} \cdot a_{SO_4^{2-}}}{a_{Al(SO_4)_2^-}} \qquad (11)$$

Equation (11) can be written as follows:

$$\log \frac{[AlSO_4^+][SO_4^{2-}]}{[Al(SO_4)_2^-]} - \frac{4A\sqrt{\mu}}{1+\sqrt{\mu}} = \log K_1 - b\mu \tag{12}$$

Taking a number of solutions with different ionic strengths and plotting LHS of equation (12) 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 $Al_2(SO_4)_3$ in $H_2SO_4$, the total aluminium is present as $Al^{3+}$, $AlSO_4^+$ and $Al(SO_4)_2^-$ ions. By the process outlined below the value of $Al(SO_4)_2^-$ need not be neglected while calculating $[Al^{3+}]$ as suggested by Sharma and Prasad[1].

At lower concentrations, the values 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 equ. (12), when we get a ratio of $[AlSO_4^+]$ to $[Al(SO_4)_2^-]$. The values of $[Al^{3+}]$, $[AlSO_4^+]$ and $[Al(SO_4)_2^-]$ can be found out with the help of equations (7), (8) and (13), *i.e.*

$$\frac{[AlSO_4^+]}{[Al(SO_4)_2^-]} = K^1 \tag{13}$$

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

$$\mu = \tfrac{1}{2}[H^+] + \tfrac{1}{2}[HSO_4^-] + \tfrac{1}{2}[AlSO_4^+] + \tfrac{1}{2}[Al(SO_4)_2^-] + 2[SO_4^{2-}] + 2[Hg_2^{2+}] + 4.5[Al^{3+}] \tag{14}$$

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 $AlSO_4^+$, *i.e.*

$$K_2 = \frac{a_{Al^{3+}} \cdot a_{SO_4^{2-}}}{a_{AlSO_4^+}}$$

$$= \frac{[Al^{3+}][SO_4^{2-}]}{[AlSO_4^+]} \times \frac{f_{Al^{3+}} \cdot f_{SO_4^{2-}}}{f_{AlSO_4^+}} \tag{15}$$

Equation (15) reduces itself to

$$\log \frac{[Al^{3+}][SO_4^{2-}]}{[AlSO_4^+]} - \frac{12A\sqrt{\mu}}{1+\sqrt{\mu}} = \log K_2 - B_1\mu \tag{16}$$

where $B_1 = B_{Al^{3+}} + B_{SO_4^{2-}} - B_{AlSO_4^+}$.

Taking a number of solutions of different ionic strengths and plotting LHS of equation (16) against μ, we get linear plots at all the four temperatures. The values of $K_2$ and $B_1$ have been obtained from these plots at 5°, 15°, 25° and 35°C.

A plot of log $K_2$ against 1/T is linear. The value of ΔH has been found from

TABLE 1
EXPERIMENTAL RESULTS
Temperature: 5°C ± 0.05°C

Dissociation $AlSO_4^+ \rightleftarrows Al^{3+} + SO_4^{2-}$, $K_2(A) = \frac{[Al^{3+}][SO_4^{2-}]}{[AlSO_4^+]}$

| $C_1 \times 10^4$ | $C_2 \times 10^4$ | E in abs m.v. | $[SO_4^{2-}] \times 10^4$ | $[Al^{3+}] \times 10^4$ | $[AlSO_4^+] \times 10^4$ | $[Al(SO_4)_2^-] \times 10^4$ | $\mu \times 10^4$ | $\log K_2(A) - \frac{12A\sqrt{\mu}}{1+\sqrt{\mu}}$ |
|---|---|---|---|---|---|---|---|---|
| 11.52 | 8.64 | 147.70 | 25.29 | 1.62 | 20.67 | 0.75 | 88.23 | –4.210 |
| 12.96 | 9.72 | 144.42 | 26.59 | 1.03 | 23.97 | 0.93 | 90.50 | –4.455 |
| 14.40 | 10.80 | 141.34 | 28.76 | 1.08 | 28.19 | 1.26 | 96.96 | –4.487 |
| 17.28 | 12.96 | 136.07 | 32.55 | 1.76 | 30.22 | 1.74 | 111.12 | –4.285 |
| 20.16 | 15.12 | 131.42 | 37.95 | 4.29 | 33.15 | 2.87 | 136.68 | –3.927 |

TABLE 2
EXPERIMENTAL RESULTS
Temperature :15°C ± 0.05°C

| $C_1 \times 10^4$ | $C_2 \times 10^4$ | E in abs m.v. | $[SO_4^{2-}] \times 10^4$ | $[Al^{3+}] \times 10^4$ | $[AlSO_4^+] \times 10^4$ | $\mu \times 10^4$ | $\log K_2(A) - \frac{12A\sqrt{\mu}}{1+\sqrt{\mu}}$ |
|---|---|---|---|---|---|---|---|
| 10.80 | 14.40 | 150.11 | 26.96 | 0.54 | 25.97 | 92.85 | –4.779 |
| 12.96 | 17.28 | 144.70 | 31.17 | 2.20 | 28.80 | 111.98 | –4.198 |
| 15.12 | 20.16 | 140.12 | 35.49 | 4.11 | 31.26 | 132.50 | –3.951 |
| 17.28 | 23.04 | 136.10 | 41.31 | 8.66 | 30.10 | 166.65 | –3.611 |

the slope of this plot. The values of G and ΔS have been found from well known equations. These values are tabulated in Table 1.

TABLE 3
EXPERIMENTAL RESULTS
Temperature 25°C ± 0.05°C

| $C_1 \times 10^4$ | $C_2 \times 10^4$ | E in abs m.v. | $[SO_4^{2-}] \times 10^4$ | $[Al^{3+}] \times 10^4$ | $[AlSO_4^+] \times 10^4$ | $\mu \times 10^4$ | $\log K_2(A) - \frac{12A\sqrt{\mu}}{1+\sqrt{\mu}}$ |
|---|---|---|---|---|---|---|---|
| 12.96 | 9.72 | 162.41 | 24.08 | 0.0235 | 22.79 | 85.09 | –6.121 |
| 14.40 | 10.80 | 159.30 | 25.44 | 0.109 | 25.03 | 90.08 | –5.485 |
| 17.28 | 12.96 | 153.76 | 29.29 | 1.64 | 27.10 | 107.76 | –4.326 |
| 20.16 | 15.12 | 149.01 | 34.77 | 5.63 | 28.05 | 138.67 | –3.800 |
| 23.04 | 17.28 | 145.01 | 39.74 | 9.12 | 28.38 | 166.83 | –3.593 |

TABLE 4
Temperature 35°C ± 0.05°C

| $C_1 \times 10^4$ | $C_2 \times 10^4$ | E in abs m.v. | $[SO_4^{2-}] \times 10^4$ | $[Al^{3+}] \times 10^4$ | $[AlSO_4^+] \times 10^4$ | $\mu \times 10^4$ | $\log K_2(A) - \frac{12A\sqrt{\mu}}{1+\sqrt{\mu}}$ |
|---|---|---|---|---|---|---|---|
| 14.40 | 10.80 | 167.11 | 25.75 | 1.89 | 21.60 | 99.35 | –4.212 |
| 17.28 | 12.96 | 161.50 | 30.34 | 5.22 | 22.24 | 125.64 | –3.775 |
| 20.16 | 15.12 | 156.79 | 35.45 | 9.43 | .21.55 | 156.71 | –3.502 |
| 23.04 | 17.28 | 152.86 | 39.59 | 12.76 | 21.49 | 182.66 | –3.370 |

TABLE 5
FINAL RESULTS
Dissociation $AlSO_4^+ \rightleftarrows Al^{3+} + SO_4^{2-}$

| Temp. in °C | Values of $K_2$ | | ΔH cal $mol^{-1}$ | ΔG cal $mol^{-1}$ | ΔS cal $deg^{-1}$ $mol^{-1}$ |
|---|---|---|---|---|---|
| | Sharma and Prasad's | Present work | | | |
| 5 | $2.51 \times 10^{-2}$ | $3.98 \times 10^{-6}$ | 13600 ± 150 | 6868.4 | 24.2 ± 0.5 |
| 15 | $1.78 \times 10^{-2}$ | $6.31 \times 10^{-6}$ | 13600 ± 150 | 6851.9 | 23.4 ± 0.5 |
| 25 | $1.26 \times 10^{-2}$ | $2.51 \times 10^{-6}$ | 13600 ± 150 | 7635.2 | 20.0 ± 0.5 |
| 35 | $0.83 \times 10^{-2}$ | $1.78 \times 10^{-5}$ | 13600 ± 150 | 6693.6 | 22.4 ± 0.5 |

The dissociation constant of $AlSO_4^+ \rightleftarrows Al^{3+} + SO_4^{2-}$ determined by an entirely different method[6] at 29–30°C is higher than our values.

Our values of $K_2$ are of the same order as that of[7,8]

$$CrSO_4^+ = Cr^{3+} + SO_4^{2-}$$

and of[8]

$$InSO_4^+ \rightleftarrows In^{3+} + SO_4^{2-}.$$

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