

## The Solubility of Potassium Sulfate in Thermodynamic view

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### ABSTRACT

The solubility of K<sub>2</sub>SO<sub>4</sub> in water at 25°C was determined. Comparing the value of thermodynamic solubility product constant, K<sub>sp</sub>(th), ( $K_{sp}(th) = \exp(-\Delta G_{diss}^{\circ} / RT)$ ) of the mentioned salt to the value of concentration solubility product, K<sub>sp</sub>(c) which is obtained from the observed solubility, s/molL<sup>-1</sup>,  $K_{sp}(c) = 4s^3$ , revealed a great difference. The difference can be satisfactorily explained using Debye- Hückel law and ion association phenomenon.

**Keywords:** Solubility product; Activity coefficient; Non ideality

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### INTRODUCTION

Comparative studies of aqueous electrolyte solutions generally always require consideration of non- ideality and ion- association. It is vital, therefore, that one regards these phenomena in order to interpret the related experimental data. A strong electrolyte solution deviate, partly by non-ideality arising from activity coefficients (physical factor) and partly by ion- association (chemical factor) from ideality. The non-ideality contribution respect to the physical factor could be evaluated by activity coefficients which can be estimated upon some theoretical models [1-5]. The ion- association contribution, in turn, can be studied both theoretically and experimentally by using several approaches [6-14].

When the concentration of an electrolyte solution tends toward zero, the ions are

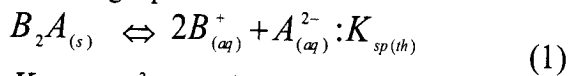
sufficiently far apart that coulombic interactions between them are negligible. Under these circumstance the ions behavior is independent from each other and the electrolyte behaves almost as an ideal solution. As the concentration increases, the average distance between the ions decreases, so interactions between them become considerable and the solution becomes progressively less ideal. In addition, the ion- solvent interactions that are present even in the ideal solution also become increasingly modified as the concentration increases, again making a progressively increasing contribution to non- ideality. The effects of non- ideality and ion- association can be observed from the way in which certain properties of the solution, such as its molar conductivity, vapour pressure, ... vary with concentration.

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## BACKGROUND

Consider an ionic compound such as  $B_2A$  which is composed of  $2B^+$  and  $A^{2-}$  ions and assume that its solubility in water at room temperature is fairly small. Therefore, in saturated solution of this ionic compound,  $B_2A$ , one can consider the following equilibrium



$$K_{sp(th)} = a_{B^+}^2 a_{A^{2-}}; (a_i = \text{activity of ion } i)$$

$$K_{sp(th)} = \exp(-\Delta G_{diss}^\circ / RT) \quad (2)$$

$$\Delta G_{diss}^\circ = \Delta H_{diss}^\circ - T \Delta S_{diss}^\circ \quad (3)$$

Where  $\Delta G_{diss}^\circ$ ,  $\Delta H_{diss}^\circ$  and  $\Delta S_{diss}^\circ$  represent standard Gibbs free energy, standard enthalpy and standard entropy change related to the equilibrium (1).

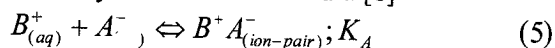
On the other hand, one can consider the estimated solubility product,  $K_{sp(est)}$ , of equilibrium (1) as follow

$$K_{sp(est)} = [B^+]^2 [A^{2-}] f_+^2 f_- \quad (4)$$

where  $[i]$  represents the molarity of species  $i$  in the solution and  $f_i$  denotes the activity coefficient of that species in the same solution. It is worthwhile to denote that the ion- association phenomenon has been neglected in introducing equation (4) with the assumption that  $f_+$  and  $f_-$  can be estimated upon a suitable model, such as Debye- Hückle theory.

For many ionic compounds, it has been seen that there is a considerable difference among the concentration solubility product,  $K_{sp(c)} = 4s^3$ , estimated solubility product,  $K_{sp(est)}$  and thermodynamic solubility product,  $K_{sp(th)}$ , and almost always  $K_{sp(c)}$  is greater than  $K_{sp(th)}$  and  $K_{sp(est)}$  [15,16].

One way of explaining the difference, is to consider the non ideality and ion- association phenomena in electrolyte solutions. For many decades ion- association in electrolyte solutions has been an area of active research interest [6-20]. Bjerum theoretical approach provides following results for association constant,  $K_A$ , of ion- pair formation in dilute solutions of electrolytes with  $B_2A$  formula [6]



$$K_A = \frac{4\pi N a^3 b^3}{1000} Q_{(b)} \quad (6)$$

$$Q_{(b)} = \int_0^{\infty} e^{-x} x^{-4} dx \quad (7)$$

$$b = \frac{|z_+ z_-| e^2}{a \epsilon k T}; x = \frac{|z_+ z_-|}{r \epsilon k T} \quad (8)$$

where,  $N$  is Avogadro constant,  $a$  is the closest of approach of ions,  $\epsilon$  represents the dielectric constant,  $k$  is Boltzmann constant,  $T$  denotes temperature in Kelvin and  $B^+ A^-$  refers to the respective ion- pair. On the other hand, Fuoss theoretical approach leads to the contact ion- pair and the following expression for  $K_A$  [6, 11]

$$K_A = c a^3 e^{c'/a c T} \quad (9)$$

where  $a$  is the parameter of the closest approach of ions in cm,  $c = 2.522 \times 10^{21}$  and  $c' = 1.66 \times 10^{-3}$

## EXPERIMENTAL

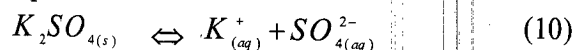
$K_2SO_4$  and other chemicals were purchased from Merck Company and used without further purification. The saturated solution of  $K_2SO_4$  in deionized water was prepared at  $25.0^\circ C$ , and then the solubility of it in water was determined using Solvent Evaporating method. Our experimental results are given in table 1.

Table 1. Solubility,  $s$ , ( $\text{mol L}^{-1}$ ) of  $K_2SO_4$ , in water at  $25.0^\circ C$  (using solvent evaporating method)

Iteration	Solubility, $s$ , $\text{mol L}^{-1}$
1	0.7035
2	0.6955
3	0.6944
4	0.7001
5	0.7024
6	0.7001
Average $0.6993 \pm 0.0033 \text{ mol L}^{-1}$	

## DISCUSSION

In the saturated solution of  $K_2SO_4$  at constant temperature, we can assume the following equilibrium



Denoting the solubility of  $K_2SO_4$  in equilibrium (10) by  $s \text{ mol L}^{-1}$ , then the concentration solubility product of it is

$$K_{sp(c)} = [K^+]^2 [SO_4^{2-}] = [2s]^2 [s] = 4s^3 \quad (11)$$

Inserting the value of experimental solubility of K<sub>2</sub>SO<sub>4</sub>, 0.6993 mol L<sup>-1</sup>, (table 1) in the equation (11), we get

$$K_{sp}(c) = 1.368 \text{ mol}^3 \text{ L}^{-3} \quad (\text{at } 25.0^\circ\text{C})$$

Now, we evaluate the thermodynamic solubility product, K<sub>sp</sub>(th), based on the data of table (2) and equations (2) and (3).

**Table2.** Thermodynamic functions of K<sub>(aq)</sub><sup>+</sup>, SO<sub>4(aq)</sub><sup>2-</sup> and K<sub>2</sub>SO<sub>4(s)</sub> at 298 K

Species	$\Delta H_f^0 / kJ$ <i>mol</i> <sup>-1</sup>	$S^0 / JK$ <sup>1</sup> <i>mol</i> <sup>-1</sup>	$\Delta G_f^0 / kJ$ <i>mol</i> <sup>-1</sup>	Ref.
K <sub>(aq)</sub> <sup>+</sup>	-252.38	102.5	-283.27	[21,23]
SO <sub>4(aq)</sub> <sup>2-</sup>	-909.27	20.1	-744.53	[21,23]
K <sub>2</sub> SO <sub>4(s)</sub>	-1434.00	176.0	-1316.00	[23]

$$\begin{aligned} \Delta H_{diss}^{\circ} &= [2\Delta H_{f(K^+)}^{\circ} + \Delta H_{f(SO_4^{2-})}^{\circ}] - \Delta H_{f(K_2SO_4)}^{\circ} \\ &= [2 \times (-252.38) + 1 \times (-909.27)] - [1 \times (-1434.00)] \\ &= 19970 \text{ J mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta S_{diss}^{\circ} &= (2 \times 102.5 + 20.1) - (176.0) \\ &= 49.1 \text{ JK}^{-1} \text{ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta G_{diss}^{\circ} &= \Delta H_{diss}^{\circ} - T \Delta S_{diss}^{\circ} \\ &= 19970 \text{ J mol}^{-1} - 298.15 \text{ K} \times 49.1 \text{ JK}^{-1} \text{ mol}^{-1} \\ &= 5331 \text{ J mol}^{-1} \end{aligned}$$

$$\begin{aligned} K_{sp(th)} &= \exp(-\Delta G_{diss}^{\circ} / RT) \\ &= 0.1164 \end{aligned}$$

As we can see, the value of K<sub>sp</sub>(th) = 0.1164 is quite different from K<sub>sp</sub>(c) = 1.368. The difference is due to the non ideality and ion-association phenomena.

The non ideality of ions in the solution can be taken into account by estimating activity coefficients, *f*<sub>±</sub>. Several equations are

introducing for estimating activity coefficient of ions in aqueous electrolyte solution. Here, we look to the semi empirical extended Debye-Hückle equation in the following form:

$$\log f_{\pm} = \frac{0.509 z_+ z_- \sqrt{I}}{1 + 0.324 a_{\pm} \sqrt{I}} + 0.2 \sqrt{I} \quad (\text{at } 25.0^\circ\text{C}) \quad (12)$$

where  $a_{\pm} = (a_+ + a_-) / 2$  and a<sub>+</sub> or a<sub>-</sub> is the size parameter of considered ion in angstrom, °A. For K<sub>2</sub>SO<sub>4</sub> (aq), we take  $a_{\pm} = (3 + 4) / 2 = 3.5^\circ\text{A}$

[12].  
So

$$\log f_{\pm} (K_2SO_4, aq) = -\frac{1.018 \sqrt{I}}{1 + 1.134 \sqrt{I}} + 0.2 \sqrt{I} \quad (13)$$

I is ionic strength and I = 3s for the saturated solution of K<sub>2</sub>SO<sub>4</sub>, while s represents the solubility of K<sub>2</sub>SO<sub>4</sub> in mol L<sup>-1</sup>. After table(1), s = 0.6993 mol L<sup>-1</sup>, so,  $\sqrt{I} = 1.4484$  and

$$\log f_{\pm} (K_2SO_4, aq) = -\frac{1.4745}{2.6425} + 0.2897 = -0.2683$$

$$\Rightarrow f_{\pm} = 0.5391$$

$$K_{sp(est)} = 4s^3 f_{\pm}^3 = 0.2143$$

As we can see, the calculated K<sub>sp</sub>(est) is nearly two times K<sub>sp</sub>(th) = 0.1164. This difference can be attributed to the ion association phenomenon in the saturated solution of K<sub>2</sub>SO<sub>4</sub> at 25.0°C, if the equation (12) could be reasonable in this condition.

## CONCLUSION

Saturated aqueous solution of K<sub>2</sub>SO<sub>4</sub> is far from ideality. The non- ideality of the solution may be interpreted as due partly to physical (activity coefficients) and partly to chemical (ion-association) factors and these contributions do predict a concordant fit of experimental data. The solubility of K<sub>2</sub>SO<sub>4</sub> could be divided in three contributions; one,  $\sqrt[3]{K_{sp(th)} / 4} = 0.3076 \text{ mol L}^{-1}$ , the other,  $[K^+SO_4^{2-}]_{i-p} = 0.2000 \text{ mol L}^{-1}$  and the physical factor contribution = 0.1917 mol L<sup>-1</sup>. The percentage of each contribution is 44%, 28.5% and 27.5% respectively.

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