

# Study of solubility equilibrium biology essay



**ASSIGN  
BUSTER**

The solubility product constant of potassium hydrogen tartrate in water and its dependence on temperature were investigated in this experiment. The solubility product constant was determined at different temperatures through acid-base titration against NaOH. A linear graph was obtained by plotting  $\ln K_{sp}$  against  $1/T$  and a positive correlation between temperatures and solubility product constant was observed. This study concluded that the solubility product constant of potassium hydrogen tartrate is dependent only on temperature.

## Introduction

The aim of this experiment is to investigate the solubility product constant of potassium hydrogen tartrate in water and its dependence on temperature. Solubility is often defined as the amount of substance required to obtain a saturated solution. Therefore, only a small amount of potassium hydrogen tartrate ( $KHC_4H_4O_6$ ) is needed to produce a saturated solution as it has limited solubility in water.

In a saturated solution, the rate of the dissociation of the solid is the same as the rate of the aqueous ions forming the solid compound; the solution is known to be at equilibrium.

The equilibrium equation for  $KHC_4H_4O_6$  in the solution can be written as:

The constant for the equilibrium equation can be expressed as:  $K_{sp} = [K^+][HC_4H_4O_6^-]$ .

This constant is also known as the solubility product constant ( $K_{sp}$ ) which has a fixed value for a given system at constant temperature. Thus, by

finding out the concentration of the ions dissolved, the solubility product constant for  $\text{KHC}_4\text{H}_4\text{O}_6$  can be determined.

From the equation above, the dissociation of  $\text{KHC}_4\text{H}_4\text{O}_6$  will produce equal amount of potassium ions ( $\text{K}^+$ ) and hydrogen tartrate ions ( $\text{HC}_4\text{H}_4\text{O}_6^-$ ). Thus, by obtaining the concentration of one of the ions, the concentration of the other ion can be derived and the solubility product constant can be calculated. As  $\text{HC}_4\text{H}_4\text{O}_6^-$  behaves like a weak acid, its concentration can be determined by acid-base titration using  $\text{NaOH}$ , a strong base as the titrant, with phenolphthalein as the indicator. As  $\text{NaOH}$  and  $\text{HC}_4\text{H}_4\text{O}_6^-$  react with each other in 1: 1 ratio, the amount of  $\text{NaOH}$  used in the titration will be equal to the amount of  $\text{HC}_4\text{H}_4\text{O}_6^-$  present in the solution.

While  $K_{sp}$  is fixed at a certain condition, changes in temperature will affect the value of  $K_{sp}$ . According to the van't Hoff equation, the value of  $K_{sp}$  is related to the change in Gibbs free energy and can be expressed as:

From the equation, the solubility product constant depends on three variables which are the change in enthalpy, the change in entropy and the temperature. The change in entropy and enthalpy with respect to temperature were stated to be insignificant due to the similar heat capacities of the product and reactants. This suggests a linear trend between the remaining variable and  $K_{sp}$  [1]. Therefore, a graph of natural logarithm of  $K_{sp}$  versus the reciprocal of temperature can be plot which the gradient of the graph can be used to calculate the enthalpy change and the y-intercept for the entropy change. Thus, the relationship between  $K_{sp}$  and temperature can be observed.

## Experimental Procedure

Dried  $\text{KHC}_8\text{H}_4\text{O}_4$  (0.5002 g) was prepared in a 250 mL conical flask with the help of an analytical balance. Deionized water (25.0 mL) was added into the flask and a standard solution of  $\text{KHC}_8\text{H}_4\text{O}_4$  was obtained. The prepared solution was then titrated against an unknown concentration of NaOH to the endpoint, with phenolphthalein as the indicator. The volume of NaOH used was recorded. The entire procedure was then repeated with different masses  $\text{KHC}_8\text{H}_4\text{O}_4$  (0.5039 g, 0.5033 g). The concentration of the NaOH was calculated from the volume of NaOH used and tabulated in Table 1.

A saturated  $\text{KHC}_4\text{H}_4\text{O}_6$  solution was prepared by adding one gram of  $\text{KHC}_8\text{H}_4\text{O}_4$  into a 250 mL conical flask, containing 100.0 mL of deionized water. The flask was swirled for five minutes and put to rest with occasional swirling for another five minutes at room temperature. At the end of ten minutes, the solution was then filtered and the supernatant was collected in a dry 250 mL conical flask. Concurrently, the temperature of the solution in the filter funnel was recorded. Two portions of 25.0 mL of the filtered solution were then pipetted into two separate 250 mL conical flasks. The two solutions were titrated against the 0.7070M NaOH solution to the endpoint, with phenolphthalein as the indicator. The volume of the NaOH used was recorded. The procedure was then repeated for different temperatures.

For temperature above room temperature, a hot water bath was prepared in a one litre beaker on a hotplate stirrer. The saturated  $\text{KHC}_4\text{H}_4\text{O}_6$  solution was prepared in the same way but was placed in a hot water bath with constant stirring, using a stir bar. The solution was put aside with occasional monitoring until a constant temperature was observed. Next, the solution

was decanted in small amount into a dry conical flask. The temperature of the solution in the filter funnel was recorded concurrently. Three portions of 25.0 mL of the filtered solution were then pipetted into three separate 250 mL conical flasks.

For temperature below room temperature, an ice-water bath was prepared in a one litre beaker. The solution was also prepared in the same way as the previous procedure and was placed into the ice-water bath. The solution was cooled until the solution stabilized at a certain temperature. The solution was then filtered and the temperature of the solution in the filter funnel was recorded. Three portions of 25.0 mL of the filtered solution were then pipetted into three separate 250 mL conical flasks similar to the above room temperature setup.

The six solutions were then placed aside for it to return to room temperature and then titrated against the standardized NaOH. The solutions were titrated the same way as the titration done at room temperature. The volume of NaOH used was recorded for the different solutions were recorded. The average volume of NaOH used for the same temperature was then calculated and tabulated in Table 2.

## **Data Treatment and Analysis**

The calculations of  $[\text{HC}_4\text{H}_4\text{O}_6^-]$ ,  $[\text{K}^+]$  and  $K_{sp}$  at 302.15K:

$$[\text{NaOH}] = 7.070 \times 10^{-2} \text{ mol L}^{-1}$$

$$\text{Amount of NaOH used} = (7.070 \times 10^{-2} \text{ mol L}^{-1}) (1.2825 \times 10^{-2} \text{ L}) = 9.067 \times 10^{-4} \text{ mol}$$

Amount of  $\text{HC}_4\text{H}_4\text{O}_6^-$  = Amount of NaOH used =  $9.067 \times 10^{-4}$  mol

$[\text{HC}_4\text{H}_4\text{O}_6^-] = [\text{K}^+] = 9.067 \times 10^{-4} / (0.0250 \text{ L}) = 3.63 \times 10^{-2} \text{ mol L}^{-1}$

$K_{sp} = [\text{K}^+][\text{HC}_4\text{H}_4\text{O}_6^-] = (3.63 \times 10^{-2} \text{ mol L}^{-1})^2 = 1.32 \times 10^{-3}$

The calculated value of  $[\text{K}^+]$ ,  $[\text{HC}_4\text{H}_4\text{O}_6^-]$  and  $K_{sp}$  were tabulated into the table below:

Table 2: Determination of  $K_{sp}$  of  $\text{KHC}_4\text{H}_4\text{O}_6$  at different temperature

**Temperature / K**

**Average Vol. of NaOH used / L**

**Amount of NaOH used / mol**

**$[\text{HC}_4\text{H}_4\text{O}_6^-] / \text{mol L}^{-1}$**

**$[\text{K}^+] / \text{mol L}^{-1}$**

**$K_{sp}$  of  $\text{KHC}_4\text{H}_4\text{O}_6$**

285.15

$7.4750 \times 10^{-3}$

$5.327 \times 10^{-4}$

$2.13 \times 10^{-2}$

$2.13 \times 10^{-2}$

$4.54 \times 10^{-4}$

294.15

1.  $0.075 \times 10^{-2}$

7.  $180 \times 10^{-4}$

2.  $87 \times 10^{-2}$

2.  $87 \times 10^{-2}$

8.  $25 \times 10^{-4}$

302. 15

1.  $2825 \times 10^{-2}$

9.  $0.67 \times 10^{-4}$

3.  $63 \times 10^{-2}$

3.  $63 \times 10^{-2}$

1.  $32 \times 10^{-3}$

309. 15

1.  $6375 \times 10^{-2}$

1.  $158 \times 10^{-3}$

4.  $63 \times 10^{-2}$

4.  $63 \times 10^{-2}$

2.  $14 \times 10^{-3}$

320. 15

2.  $2.375 \times 10^{-2}$

1.  $5.82 \times 10^{-3}$

6.  $3.3 \times 10^{-2}$

6.  $3.3 \times 10^{-2}$

4.  $0.00 \times 10^{-3}$

Based on the temperature and  $K_{sp}$  value obtained in Table 1, values of  $1/T$  and  $\ln K_{sp}$  were calculated and tabulated in Table 3. A graph was plotted based on the values:

Figure 1: Graph of  $K_{sp}$  versus  $1/T$

From Figure 1, the gradient and y-intercept was obtained as shown in Table 4.

The enthalpy change and entropy change was calculated based on the van't Hoff equation:

$$\text{Gradient} = - (\Delta H / R) = -5692.06$$

$$\text{Standard deviation of gradient: } \pm 99.87$$

$$= - (-5692.06 \times 8.314) \pm (99.87 \times 8.314) = (47.32 \pm 0.83) \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$\text{Y-intercept} = (\Delta S / R) = 12.25 \pm 0.33$$

$$\text{Standard deviation of Y-intercept} = \pm 0.33$$



$$= (12.25 \times 8.314) \pm (0.33 \times 8.314) = (101.85 \pm 2.74) \text{ J K}^{-1} \text{ mol}^{-1}$$

The standard error of regression was found to be 0.0295.

(Number of measurements = 6, Degree of Freedom = 4)

## Results and Discussion

From the data obtained, the calculated values of  $\Delta H$  and  $\Delta S$  were  $(47.3 \pm 0.83) \text{ kJ K}^{-1} \text{ mol}^{-1}$  and  $(101.85 \pm 2.74) \text{ J K}^{-1} \text{ mol}^{-1}$  respectively.  $K_{sp}$  of  $\text{KHC}_4\text{H}_4\text{O}_6$  was found to be  $1.32 \times 10^{-3}$  at 302.15K. It was observed that a linear graph was obtained upon plotting  $\ln K_{sp}$  against the reciprocal of T. The increase in temperature was also found to correlate with the increase of  $K_{sp}$  values. The literature  $K_{sp}$  value for  $\text{KHC}_4\text{H}_4\text{O}_6$  is  $3.8 \times 10^{-4}$  at 291.15K. [2] The approximated  $K_{sp}$  value that corresponds to 291.15k based on experimental data was calculated to be  $6.755 \times 10^{-4}$  as shown in the Appendices.

### Linear Relationship between T and $K_{sp}$

Based on figure 1, a linear model was observed between the reciprocal of T and the natural logarithm of  $K_{sp}$ . This was supported by the R-square value of 0.99 which greatly suggests a linear trend from the experimental data plotted. The standard error of regression obtained from the experiment was found to be 0.0295, which indicates a good fit among the experimental values obtained, corresponding to a good precision of the experimental data. Thus from the linear trend, the claim of insignificant changes of enthalpy and entropy due to temperature changes was valid. Therefore, the assumption that the value of  $K_{sp}$  is dependent only on temperature at which the dissolution occurs can be established.

## Comparison of Literature values

The estimated  $K_{sp}$  value based on experimental data was  $6.755 \times 10^{-4}$  at 291.15K and was found to be 43.75% higher than the literature value ( $3.8 \times 10^{-4}$ ) [2]. The difference could be accounted to the limitation of this experiment. As the experiment was carried out in different temperature, one of the limitations was due to the apparatus used. The volumetric glass pipette used was calibrated at 20 , thus at other temperature, expansion or contraction might occur leading to the inaccurate volume transferred for titration after the filtering process. Another source of error was noted to be the temperature fluctuation during the filtering process. Although the solution were decant in small portions to minimize errors, rapid increase of the temperature for the cold temperature reading was observed. This corresponds to the increase in the ions concentration dissolved in the solution, thus resulting in a higher value of  $K_{sp}$ . Despite the percentage difference of 43.75%, the difference between both values was actually small due to the fact that the  $K_{sp}$  of  $KHC_4H_4O_6$  is a very small value. When the uncertainty of the enthalpy change and entropy change was taken into account, the experimental  $K_{sp}$  value was assumed to be between  $3.446 \times 10^{-4}$  and  $1.324 \times 10^{-3}$ (Refer to Appendices). The literature value was noted to be within this range, thus the experimental data do agree with the theoretical value of  $KHC_4H_4O_6$ .

## Change of Enthalpy and Entropy

The change of enthalpy from the reaction was found to be  $(47.3 \pm 0.83)$  kJ  $K^{-1} mol^{-1}$ . The positive enthalpy change means that the dissolution of

KHC<sub>4</sub>H<sub>4</sub>O<sub>6</sub> was an endothermic process where heat was absorbed during the process. This was expected as the dissolution breaks up the stronger ionic bonds within KHC<sub>4</sub>H<sub>4</sub>O<sub>6</sub> and weaker bonds between the water molecules and the ions was formed. These resulted in a positive net change for enthalpy for the reaction, which is consistent with the positive enthalpy change derived from the experimental data. The change of entropy was found to be  $(101.85 \pm 2.74) \text{ J K}^{-1} \text{ mol}^{-1}$ . As entropy was often defined as a measure of disorder, the positive entropy can be explained with the increased disorder brought about when the when KHC<sub>4</sub>H<sub>4</sub>O<sub>6</sub> dissolved into ions.

As the value of enthalpy change was much larger than the entropy change, in order to get a larger value of  $\ln K$  based on the van't Hoff equation, higher temperature was required. This coincide with high temperature favors endothermic process such as dissolution of KHC<sub>4</sub>H<sub>4</sub>O<sub>6</sub>, thus it can be concluded that temperature have a positive correlation with  $K_{sp}$ .

## Conclusion

$K_{sp}$  have a linear relationship with temperature for KHC<sub>4</sub>H<sub>4</sub>O<sub>6</sub>. The temperature dependent of enthalpy change and entropy change was found to be insignificant for the dissolution of KHC<sub>4</sub>H<sub>4</sub>O<sub>6</sub>. As dissolution is an endothermic process, temperature has a positive correlation with  $K_{sp}$ , thus higher temperature allow more KHC<sub>4</sub>H<sub>4</sub>O<sub>6</sub> to dissolve. This concluded that solubility product constant of potassium hydrogen tartrate is dependent only on temperature.