



Determination of the Solubility Product Constant of an Organic Salt

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Purpose of the Experiment

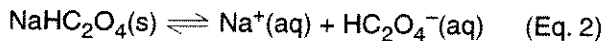
Determine the solubility and solubility product constant of potassium hydrogen tartrate by titrimetry.

Background Information

A complete characterization of a chemical system involving substances dissolved in water includes studying the relevant equilibria. For the generalized chemical reaction $aA + bB \rightleftharpoons cC + dD$, the equilibrium constant expression is:

$$K_{\text{eq}} = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (\text{Eq. 1})$$

In the case of an acid salt, such as sodium hydrogen oxalate monohydrate ($\text{NaHC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) dissolving in water, an equilibrium is established among solid sodium hydrogen oxalate (NaHC_2O_4), sodium ion (Na^+), and hydrogen oxalate ion (HC_2O_4^-), as shown in Equation 2.



A quantitative characterization of this equilibrium would involve determination of the amount of dissolved $\text{NaHC}_2\text{O}_4(\text{aq})$ in the presence of excess solid $\text{NaHC}_2\text{O}_4(\text{s})$. From Equation 2, we see that one mole of Na^+ and one mole of HC_2O_4^- would be present in solution if one mole of NaHC_2O_4 dissolved. The molar ratio of dissociated NaHC_2O_4 to Na^+ in solution to HC_2O_4^- in solution would be 1:1:1. Thus, by determining the concentration of HC_2O_4^- in solution, we can

find the amount of dissolved NaHC_2O_4 . The concentration of HC_2O_4^- in solution could be determined by the direct titration of the filtered solution with a standard NaOH solution, as hydrogen oxalate ion is a weak acid. Since the molar ratio of HC_2O_4^- to NaHC_2O_4 is 1:1, the solubility of the acid salt will be numerically equal to $[\text{HC}_2\text{O}_4^-]$.

As is the case with all equilibrium constant expressions, the amount of solid present does not affect the equilibrium concentrations, so long as some solid is present. The process involved in the dissolution of sodium hydrogen oxalate is shown in Equation 2. The concentrations of all solids are assigned a value of 1.0, and therefore the concentrations of solids do not appear in the equilibrium constant expressions.

The equilibrium constant for solids dissolving in a solvent is termed the **solubility product constant**, K_{sp} . For the reaction in Equation 2, K_{sp} is written as shown in Equation 3.

$$K_{\text{sp}} = [\text{Na}^+][\text{HC}_2\text{O}_4^-] \quad (\text{Eq. 3})$$

The true K_{sp} expression involves a correction for the behavior of ions in solution. Most ionic solutions are not dilute, and their behavior is not always ideal. The value calculated using Equation 3 is a close approximation of the actual K_{sp} .

In this experiment, you will use Equation 3 to calculate K_{sp} from the concentrations determined from the titrimetric data. We will refer to this calculated value as the solubility product constant, keeping in mind that it is really only a close approximation of the actual value.

Let's consider the following experiment, from the results of which we will determine the solubility of $\text{NaHC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and calculate its solubility product constant. A 20.00-mL sample of a filtered, saturated NaHC_2O_4 solution, at 20 °C, requires 20.38 mL of 0.1283M NaOH to reach the equivalence point. The number of moles of NaOH used can be found using Equation 4.

$$\begin{aligned} \text{number of} \\ \text{moles} &= (\text{molarity, } M)(\text{volume, L}) && \text{(Eq. 4)} \\ \text{of NaOH} &= (0.1283 \text{ mol L}^{-1})(2.038 \times 10^{-2} \text{ L}) \\ &= 2.615 \times 10^{-3} \text{ mol} \end{aligned}$$

The number of moles of NaOH added at the equivalence point is equal to the number of moles of HC_2O_4^- present in the original solution, or 2.615×10^{-3} mol. The concentration of HC_2O_4^- can be found using Equation 5.

$$\begin{aligned} [\text{HC}_2\text{O}_4^-] &= \frac{\text{number of moles} \\ &\quad \text{of } \text{HC}_2\text{O}_4^-}{\text{volume of NaHC}_2\text{O}_4 \\ &\quad \text{solution, L}} && \text{(Eq. 5)} \\ &= \frac{2.615 \times 10^{-3} \text{ mol}}{2.000 \times 10^{-2} \text{ L}} = 0.1308M \end{aligned}$$

Because of the stoichiometry in Equation 2, the concentration of Na^+ is 0.1308M, too. Therefore, the solubility of $\text{NaHC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ is 0.1308M. The relationships among concentrations and solubility are shown in Equation 6.

$$\begin{aligned} [\text{NaHC}_2\text{O}_4, \text{ (aq)}] &= [\text{Na}^+] = [\text{HC}_2\text{O}_4^-] && \text{(Eq. 6)} \\ &= \text{solubility of NaHC}_2\text{O}_4 \text{ (aq)} \end{aligned}$$

The K_{sp} of $\text{NaHC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ can be calculated using Equation 3.

$$K_{sp} = (0.1308M)(0.1308M) = 1.711 \times 10^{-2}M^2$$

Some people prefer not to add units to K_{sp} values. In such a case, the K_{sp} for this reaction would be reported as simply 1.71×10^{-2} .

In this experiment, you will determine the solubility in water of a slightly soluble salt, potassium hydrogen tartrate (KHT). You will use the solubility to calculate the solubility product constant for a filtered, saturated solution of KHT at room temperature. KHT has the

formula $\text{KHC}_4\text{H}_4\text{O}_6$ and the structure shown in Figure 1. Of the six hydrogen atoms in the molecule, only the two on the carboxylic acid groups ($-\text{COOH}$) tend to dissociate. One of these two hydrogens has been replaced by a potassium ion to form KHT, making it a monoprotic acid.

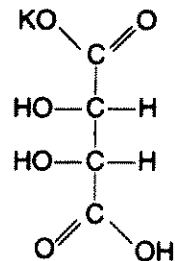
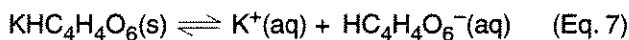


Figure 1 The structure of potassium hydrogen tartrate

The equation for KHT dissolving in water is:



The solubility product constant for this reaction is:

$$K_{sp} = [\text{K}^+][\text{HC}_4\text{H}_4\text{O}_6^-] \quad \text{(Eq. 8)}$$

You will prepare a saturated solution of KHT at room temperature. The mass of KHT and the volume of distilled water used are not critical. As long as excess solid KHT is present, the correct equilibrium concentration will be established at the existing temperature. You will stir this solution for at least 20 min to ensure saturation.

Solubility is highly temperature dependent, so it is essential that the flask not be heated during stirring. If you are using a magnetic stirrer in this experiment and the stirring motor has a tendency to become warm while operating, put several insulating layers of towel between the flask and the magnetic stirrer. The temperature must remain constant for all determinations, in order for the results to be comparable.

You will determine the amount of dissolved KHT by titrating the hydrogen tartrate ions (HT^- , a monoprotic acid) with a standard sodium hydroxide solution of known concentration, after first removing excess solid KHT by filtration. The funnel and beaker you will use in the filtration must be dry. Any water added to the filtered, saturated solution will lower the concentration of dissolved KHT.

You will then dispense a measured portion of the filtered solution from a buret, and you will titrate to the endpoint with a standard sodium hydroxide solution. The titration flask should be clean, but it does not have to be dry. The volume and concentration of the solution dispensed from the buret determine the number of

moles of HT^- present. Thus, even if the solution becomes diluted by distilled water during titration, the number of moles of HT^- will not change.

Because one mole of sodium hydroxide neutralizes one mole of HT^- ions, the number of moles of sodium hydroxide used in the titration will equal the number of moles of HT^- . You will calculate the $[\text{HT}^-]$ in the same way as $[\text{HC}_2\text{O}_4^-]$ was calculated in Equation 5. The $[\text{HT}^-]$ will be equal to $[\text{K}^+]$, which in turn will be equal to the solubility of KHT. Then you will calculate the K_{sp} for KHT, using Equation 8.

Procedure

Chemical Alert
sodium hydroxide—corrosive

Caution: Wear departmentally approved eye protection while doing this experiment.

Weigh out about 1.9 to 2.0 g of finely powdered potassium hydrogen tartrate. Transfer it to a clean 500-mL Florence flask. Add 150 mL of distilled water and a stirring bar, if you are using a magnetic stirrer. Stir with a moderate vortex for 20 minutes or more. If you are stirring with a glass rod, use a 400-mL beaker instead of a Florence flask and stir continuously.

Place a piece of dry filter paper in a dry filtering funnel. Filter the solution into a clean, dry 250-mL beaker, labeled "Determination 1." Measure the temperature of this solution and record it on your Data Sheet.

Note: If you are doing more than one determination, prepare the solution for your next determination now and leave it to stir. Continue with the solution for the present determination while the solution for your next determination is stirring.

Record the exact concentration of the assigned sodium hydroxide solution on your Data Sheet. Rinse a 50-mL buret with two 5-mL portions of distilled or deionized water, then with two 5-mL portions of your standard NaOH solution, draining the rinses through the buret tip into your waste beaker. Use a buret funnel to fill the buret with the NaOH solution. Drain some

of the solution through the buret tip into your waste beaker, until the meniscus is below the 0.00-mL graduation. Record your initial buret reading to the nearest 0.01 mL on your Data Sheet.

Rinse a second 50-mL buret with two 5-mL portions of distilled water, then with two 5-mL portions of the **filtered** KHT solution. Fill the buret with the KHT solution. Drain some KHT solution through the buret tip into your waste beaker, until the meniscus is below the 0.00-mL graduation. Record your initial buret reading to the nearest 0.01 mL on your Data Sheet.

Drain exactly 35 mL of your KHT solution from the buret into a clean, 250-mL Erlenmeyer flask labeled "Determination 1." Record your final buret reading to the nearest 0.01 mL on your Data Sheet. Add 4 drops of phenolphthalein solution. Titrate with the NaOH solution until the first faint, but permanent, pink color appears. Record your exact final buret reading on your Data Sheet.

Do a second determination by repeating the previous procedure. If time permits, do a third determination.

Dispose of all solutions according to the directions of your laboratory instructor.

Calculations

Do the following calculations for each determination and record the results on your Data Sheet.

1. Calculate the number of moles of NaOH used in your titration, using Equation 4.
2. Find the number of moles of HT^- present in the original solution, using an equation corresponding to Equation 5.
3. Calculate the concentration of HT^- in the original KHT solution in mol L^{-1} .
4. Find the concentration of K^+ in the original KHT solution in mol L^{-1} .
5. Find the solubility of KHT in mol L^{-1} . See Equation 6.
6. Calculate the average solubility of KHT in mol L^{-1} .
7. Calculate the K_{sp} of KHT in distilled water, using Equation 8.
8. Calculate the average K_{sp} for KHT.

name

section

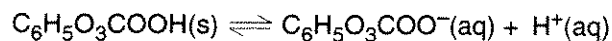
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Pre-Laboratory Assignment

1. In an appropriate source, read a discussion of the laboratory techniques used in acid-base titrations.

organic acid (gmm = 170.12). The equilibrium involved is:

2. An experiment similar to the one in this module was performed to determine the solubility and the solubility product constant of gallic acid, a monoprotic



Titration using $1.14 \times 10^{-1} \text{ M NaOH}$ were performed, and the following data were obtained.

	1	determination 2	3
temperature of solution, °C	20.2	20.4	20.1
volume of acid solution titrated, mL	25.00	22.00	20.10
volume of NaOH solution used, mL	14.61	13.02	11.73

Calculate the following:

number of moles of NaOH used

number of moles of H⁺ titrated

[H⁺] in acid solution

[C₆H₅O₃COO⁻] in acid solution

K_{sp}

average K_{sp}

solubility of acid in g per 100 mL

chemistry handbook value for solubility at 20 °C

1.15 g per 100 mL