Chemistry 1C **Name** ______________________________

Solubility Product Constant ***Partner***

Determination of a Solubility Product Constant and the Common Ion Effect[1]

Objectives

- To understand the solubility product constant, k_{sp}.
- To find the solubility product constant for a simple salt.
- To understand the common ion effect.
- To experimentally compare solubility in the absence and presence of a common ion.
- To experimentally determine the effect a common ion has on a K_{sp} value.

Discussion – Solubility Product Constant

In this experiment we will determine the solubility product constant, K_{sp}, of the slightly soluble salt potassium hydrogen tartrate, $KHC_4H_4O_6$. To demonstrate the effect of a common ion on solubility, an example of Le Chatelier's Principle, we will measure the solubility of this salt in pure water and in a solution containing KCl. We will also determine the effect a common ion has on a K_{sp} value.

A sparingly soluble salt is in equilibrium with its constituent ions in solution. In general for a salt having a formula X_aY_b, the solubility equilibrium may be expressed as:

$$X_aY_b(s) <—> aX^{n+}(aq) + bY^{m-}(aq) \tag{1}$$

The equilibrium constant for this process is called the solubility product constant, K_{sp}

$$K_{sp} = [X^{n+}]^a [Y^{m-}]^b \tag{2}$$

For example, the equilibrium expression for barium sulfate dissolving in water is represented by the equation

$$BaSO_4(s) <—> Ba^{2+}(aq) + SO_4^{2-}(aq) \tag{3}$$

And the solubility product constant, K_{sp} is expressed by the following equation

$$K_{sp} = [Ba^{2+}][SO_4^{2-}] \tag{4}$$

The value of the solubility constant depends only on temperature for a given salt and is completely independent of the quantity of the solid, undissolved salt that remains. The solubility product constant for $BaSO_4$ in pure water at 25.0°C is $1.1x10^{-10}$. If solid $BaSO_4$ is dissolved in pure water **to form a saturated solution**, then:

$$K_{sp} = [Ba^{2+}][SO_4^{2-}] = 1.1x10^{-10} \tag{5}$$

Mathematically we can write K_{sp} expressions using molar solubility, S, in place of individual ion concentrations. If we define S as the molar solubility of $BaSO_4$, then S moles of this salt dissolve in one liter of solution. In a saturated solution of pure $BaSO_4$, $[Ba^{2+}] = [SO_4^{2-}] = S$ and equation (5) can be rewritten as

$$K_{sp} = SxS = 1.1x10^{-10} \text{ therefore} \tag{6}$$

$$S = \sqrt{1.1x10^{-10}} = 1.0x10^{-5}\ M \tag{7}$$

This means that, at 25.0°C, $1.1x10^{-5}$ moles of $BaSO_4$ will dissolve in one-liter solution to produce a saturated solution. In the discussion above, we considered the case in which the salt $BaSO_4$ was dissolved in pure water. If we dissolved $BaSO_4$ in a dilute solution containing either Ba^{2+} or SO_4^{2-} ions (from another source), we have to consider the effect of the already present ions on the solubility of $BaSO_4$. Suppose we dissolve $BaSO_4$ in a 0.10 M solution of sodium sulfate. On a molecular level, there is no distinction among SO_4^{2-} ions in solution, whether they were produced from the solid $BaSO_4$ dissolving or from another salt. The solubility product constant must be satisfied for $BaSO_4$ regardless of what else is present in the solution. However, the concentration of $SO_4^{2-}(aq)$ in the solution is already 0.10 M before $BaSO_4$ was added to the solution. When substituting into the expression for K_{sp} in equation (5) we must consider the already present 0.10 M sulfate ions.

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[1] Adapted from an experiment by N. Rezaie.

$$K_{sp} = [S][S + 0.10] = 1.1\text{x}10^{-10} \text{ M} \quad (8)$$

In this case, S is the molar solubility of $BaSO_4$ in the presence of 0.10 M Na_2SO_4. The concentration of Ba^{2+} in this solution is S, but $[SO_4^{2-}] = [S] + [0.10]$. Since K_{sp} is very small, we can make the approximation $[S + 0.10] \approx 0.10$ and easily solve for $[Ba^{2+}]$:

$$[Ba^{2+}] = 1.1\text{x}10^{-9} \text{ M}, [SO_4^{2-}] \approx 0.10 \text{ M}$$

Since the only source of Ba^{2+} ion is from the dissolving of $BaSO_4(s)$, then $1.1\text{x}10^{-9}$ mol/L of $BaSO_4(s)$ must be dissolved to reach saturation in the presence of the common ion, $SO_4^{-2}(aq)$. This is approximately 10,000 times less $BaSO_4(s)$ than dissolved in one liter of pure water. The presence of the common ion already in the solvent has decreased the solubility of $BaSO_4(s)$ by five orders of magnitude.

Application to the Slightly Soluble Salt Potassium Hydrogen Tartrate

In this experiment, we will first determine K_{sp} for the salt potassium hydrogen tartrate, $KHC_4H_4O_6(s)$, in pure water. Potassium hydrogen tartrate is a slightly soluble salt and dissolves in water with the following equilibrium:

$$KHC_4H_4O_6(s) <\!\!-\!\!> K^+(aq) + HC_4H_4O_6^-(aq) \quad (9)$$

$$K_{sp} = [K^+][HC_4H_4O_6^-] \text{ or } K_{sp} = [K^+][HT^-] \text{ where } HT^- \text{ represents } HC_4H_4O_6^- \quad (10)$$

We will dissolve enough potassium hydrogen tartrate, KHT, in deionized water to **make a saturated solution**. In this solution the concentration of potassium ion is equal to the concentration of hydrogen tartrate ion. Since the hydrogen tartrate ion, HT^-, behaves as a weak acid its concentration can be determined by acid-base titration using NaOH as the titrant. Thus, the molar solubility of KHT and the value of K_{sp} can be determined. By defining S as the molar solubility of KHT then, in a saturated solution of pure KHT, $[K^+] = [HT^-] = S$ and equation (10) can be rewritten as:

$$K_{sp} = [K^+][HT^-] = S\text{x}S = S^2 \quad (11)$$

In the second part of this experiment, we will dissolve enough potassium hydrogen tartrate in a dilute solution of KCl(aq) to also make a **saturated solution of KHT**. In this case a common ion is present from the KCl(aq). Again, the concentration of HT^- can be determined by titration. However, in this case the concentration of K^+ is not equal to the concentration of HT^- as before since a significant amount of K^+ is present from the KCl. The concentration of HT^- is still S, but $[K^+] = [S] + [KCl]$ and equation (10) becomes:

$$K_{sp} = [K^+][HT^-] = ([S] + [KCl])\text{x}S \quad (12)$$

In this case, S is the molar solubility of KHT in the presence of the KCl. If the concentration of KCl(aq) is known, then K_{sp} can be determined in the presence of the common ion.

Materials

Day 1	**Day 2**
(2) 250-mL Erlenmeyer flasks with stoppers 100-mL volumetric flask Pure KHT Pure KCl (1) magnetic stirrer (1) magnetic stir bar	50-mL buret (1) 50 mL beaker 6 M NaOH (1) 25-mL pipet and pipet pump (1) 500-mL round bottom flask Phenolphthalein solution
	(2) 250-mL Erlenmeyer flasks (1) 10-mL graduated cylinder Medium grade filter paper Short stem funnel Digital Thermometer

Safety

Wear safety glasses at all times.
The 6M NaOH is corrosive. Avoid contact with skin and clothes. If contacted, wash immediately with tap water.

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Procedure Day 1

Pure KHT solution.

Weight about 0.70 g of KHT on a weighing paper. (No need to record the actual mass in your notebook; why not?) Place this powder into a 250-mL Erlenmeyer flask and add 100-ml of deionized water. Label this flask “Pure KHT”. Add a magnetic bar to this solution and stir for 25 minutes using, a magnetic stirrer and stir bar. When done, stopper this flask and store in your locker until the next lab period. Rinse and dry the magnetic stir bar.

KHT in KCl solution.

Weigh accurately about 0.08 grams of KCl into a small clean and dry 50-ml beaker. Record the mass of KCl to the nearest milligram. Add about 30 ml of DI water to the beaker to dissolve the potassium chloride and **transfer quantitatively** into your 100 ml volumetric flask. Bring the volume of the solution to the mark with DI water. Invert several times to mix and transfer the contents to a clean and dry 250-ml Erlenmeyer flask. Calculate the concentration of KCl in this solution and label the flask with the concentration and contents. To this flask add about 0.70 g of KHT (Again, no need to record the actual mass in your notebook; why not?) and stir the solution by magnetic stirrer for at least 25 minutes as before. Stopper the flask and store it in your locker until the next lab period.

Procedure Day 2

Standardization of NaOH

Dilute 1.6-1.8 ml of 6 M desk reagent NaOH solution to a total volume of about 400 mL using a clean 500-mL round bottom flask. Stopper the flask and mix thoroughly by repeatedly inverting the solution. Clean thoroughly a 50-ml buret using a little soap solution, then rinse the buret first with tap water, then with DI water and finally with three small portions (about 5 mL each) of your NaOH solution. Now fill the buret with your NaOH solution, making sure there is no air bubbles trapped in the tip of the buret. Accurately weigh, **by difference**, 0.12- 0.15 grams of potassium hydrogen tartrate into a 250-ml Erlenmeyer flask. Dissolve the acid sample in about 50-ml fresh distilled water. Add three drops of phenolphthalein indicator and titrate the sample with the NaOH solution from the buret until the first permanent appearance of light pink-color Record the initial and final buret readings to the nearest 0.05 ml for each titration. **Repeat the titration two more times**. Calculate the precise molarity of NaOH solution from your three trials.

Titration of KHT solutions in pure water

Measure and record the temperature of the KHT solution prepared last period. Obtain a clean, dry 250-mL Erlenmeyer flask and filter the solution **using a dry funnel** and medium grade filter paper (do not wet!) into the flask. Label the flask and stopper it. Using a 25-ml volumetric pipet remove a small portion of this solution to rinse the pipet. Transfer 25-ml of filtered KHT solution into a clean 250-mL Erlenmeyer flask Add 2 drops of phenolphthalein indicator to the flask. Record the initial volume of NaOH solution in the buret to the nearest 0.05 ml. Titrate the sample of KHT solution in pure water to the light pink phenolphthalein end point. Record the final volume of NaOH solution from the buret to the nearest 0.05 ml. **Repeat this titration two more times**.

Titration of KHT solutions in KCl

Measure and record the temperature of the KHT in KCl solution prepared last period. Obtain a clean, dry 250-mL Erlenmeyer flask and filter the solution **using a dry funnel** and medium grade filter paper (do not wet!) into the flask. Label the flask and stopper it. Using a dry 25-ml volumetric pipet remove a small portion of this solution to rinse the pipet. Transfer 25-ml of filtered KHT solution in KCl into a clean 250-mL Erlenmeyer flask Add 2 drops of phenolphthalein indicator to the flask. Record the initial volume of NaOH solution in the buret to the nearest 0.05 ml. Titrate the sample of KHT solution in KCl to the light pink phenolphthalein end point. Record the final volume of NaOH solution from the buret to the nearest 0.05 ml. Remember if the common ion effect is present the volume of base used should be less than in the titration of pure KHT in water. **Repeat this titration two more times**.

Clean-up

Thoroughly rinse your buret before returning it to the stockroom. Dispose of the filter paper, the titrated solutions, any unused NaOH and any left over solutions of KHT or KHT/KCl in the waste container that is provided for this experiment. (All wastes can be added to the same container.)

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Data

Day 1 – Solution preparation

Mass of KCl dissolved into the 100 mL volumetric flask ____________________

Day 2 – Titrations

1. NaOH Standardization

Trial	Volume NaOH used	Grams KHT titrated
1		
2		
3		

2. Titration of KHT in water:
Temperature of Solution:___________

Trial	Volume NaOH used
1	
2	
3	

3. Titration of KHT in KCl solution:
Temperature of Solution:___________

Trial	Volume NaOH used
1	
2	
3	

Calculations

1. Using the standardization of the NaOH data for trial 1 show how the precise molarity of the NaOH can be determined.

a) Calculated results for trial 2 ________________ and trial 3 _________________

b) Average NaOH molarity __________________________

2. Using the data from the titration of pure KHT in water, show how the molar solubility, S, of the KHT can be determined for trial 1.

a) Calculated results for trial 2 ______________ and trial 3 ______________

b) Average molar solubility ______________________

3. Using the data from the titration of KHT in KCl show how the molar solubility, S, of the KHT can be determined for trial 1 in the presence of a common ion, K^+.

a) Calculated results for trial 2 ______________ and trial 3 ______________

b) Average molar solubility in the presence of K^+ __________________

4. Using the average molar solubility found for pure KHT in water calculate K_{sp} for KHT.

5. Look up the literature value of K_{sp} for KHT. The literature value can be found on the internet with a little searching. Compare your results to the literature value by calculating a percent error. Don't be surprised if your value is significantly in error.

   a) Can you think of a reason, related to experimental conditions, that can cause your value to disagree with the literature value? (Hint: What does the value of an equilibrium constant for a given process depend upon?)

6. Compare the molar solubility of KHT in pure water to that of KHT in KCl. Calculate the percent change. Percent change = $[(S_{KCl} - S_{pure})/S_{pure}] \times 100\%$

   a) Are these results what you would expect? Why?

7. Using the molar solubility found for KHT in KCl and the calculated concentration of the KCl, calculate a K_{sp} for KHT in the KHT/KCL solution.

a) How does this value compare to your answer in 4? Do you expect them to be the same or different? Explain.

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Follow-up Questions

1. The molar solubility of Ag_2CrO_4 in water at 25 °C is 7.8×10^{-5} M.
   a) Calculate K_{sp}

   b) What is the solubility expressed as g Ag_2CrO_4 per 100 mL of solution?

2. 25 mL of 0.10 M $Pb(NO_3)_2$ is mixed with 50-mL of 0.090 M Na_2SO_4.
   a) Write an equation for a possible precipitation reaction.

   b) Under the conditions specified will a precipitate from? Show your work!