

SOLUBILITY AND THE SOLUBILITY PRODUCT CONSTANT

MATERIALS: 100 mL beakers (3); 25 mL pipet; 50 mL burets (2); 125 mL Erlenmeyer flask (2); filter funnel; 5" filter paper; phenolphthalein in dropper bottles; standardized ~0.025 M NaOH solution; saturated solution of $\text{KHC}_4\text{H}_4\text{O}_6$ which is also 0.0150 M in NaCl; saturated solution of $\text{KHC}_4\text{H}_4\text{O}_6$ which is also 0.0150 M in KCl.

PURPOSE: The purpose of this experiment is to determine a solubility product equilibrium constant, K_{sp} , and to distinguish the K_{sp} from the solubility.

LEARNING OBJECTIVES: By the end of this experiment, the student should be able to demonstrate the following proficiencies:

1. Determine the value of a K_{sp} equilibrium constant in the presence and absence of a common ion.
2. Experimentally distinguish between the solubility and the solubility product constant.
3. Use an acid-base titration to quantitatively determine the amount of a weak acid present in solution.
4. Understand the common ion effect.

DISCUSSION:

Many ionic compounds, such as NaCl, readily dissolve in water, but others have quite limited solubility. The *solubility* of a salt is the quantity or amount present in some volume of *saturated solution*, one for which an equilibrium exists between the pure solid and its dissolved and dissociated ions. Solubilities can cover a wide range of values, e.g. 36 g/100 mL (6.1 M) for NaCl, and 0.00019 g/100 mL (1.3×10^{-5} M) for AgCl, both at 25°C. Substances on the low end of the solubility range, say ≤ 0.01 M, are often described as being "insoluble" salts.

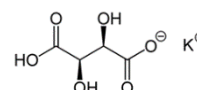
The equilibrium that exists in saturated solutions of insoluble salts is called a solubility equilibrium, and the equilibrium constant for that case is called the solubility product constant, or K_{sp} . For AgCl, these have the form



The K_{sp} is an ordinary equilibrium constant, and can be treated with the usual equilibrium tools, such as the I.C.E. (Initial, Change, Equilibrium) table for quantitative calculations. Like other equilibrium constants, it depends only on the temperature, and not on the concentrations of other dissolved substances. *Unlike* the K_{sp} , the solubility (how much dissolves) *does* depend on the presence of other substances in solution, especially for "common ions", those dissolved ions common to both the insoluble salt and another compound. It is easy to see how this works by applying LeChatelier's Principle to the equilibrium of equation 1. If we start with a saturated solution of AgCl, and add the soluble salt NaCl to the solution, the NaCl will dissolve and increase the $[\text{Cl}^-]$. By LeChatelier's Principle, the reaction equilibrium will shift left, resulting in a larger amount of the solid (undissolved) AgCl. Thus the solubility of AgCl will decrease. Since the temperature remains constant, the K_{sp} is unchanged by that action. These features are reconciled when we recognize that the $[\text{Cl}^-]$ term in the K_{sp} expression of equation 1 includes chloride ion from all sources, not just the dissolution of AgCl. Adding NaCl increased the chloride ion concentration, so the $[\text{Ag}^+]$ had to decrease, by precipitating out some AgCl (s).

K_{sp} values are often quite difficult to measure, because the concentrations of the substances involved are very small. A common way to determine them is by a precipitation titration, where one adds reagent while looking for the faint evidence of formation of the insoluble salt, signaling that the solution has become saturated. In this experiment we can use an alternate approach, because one of the ions of the insoluble salt is acidic. We can thus perform a (much easier) acid-base titration to determine the amount of that ion, and obtain the K_{sp} from that.

The insoluble salt for this experiment is potassium hydrogen tartrate, $\text{KHC}_4\text{H}_4\text{O}_6$. (This substance is well-known in kitchens as "cream of tartar", and is also an ingredient in baking powder.) The solubility equilibrium for potassium hydrogen tartrate is



In the absence of any other source of potassium ion, the $[K^+]$ will equal the $[HC_4H_4O_6^-]$, so determining the concentration of the hydrogen tartrate ion $HC_4H_4O_6^-$ by titration with a base will allow us to determine the K_{sp} . The analytical reaction to achieve that is



To illustrate the difference between the solubility and the solubility product constant, we will analyze two different saturated solutions of potassium hydrogen tartrate, one without added potassium ion, and one with potassium ion added in the form of KCl, a very soluble salt, in addition to the potassium hydrogen tartrate. In both cases, the value of the K_{sp} is given by:

$$K_{sp} = [K^+]_{tot} [HC_4H_4O_6^-] \quad (4)$$

where the subscript on the symbol $[K^+]_{tot}$ is just a reminder that it is the total potassium ion concentration that matters. But $[K^+]_{tot}$ will be different in the two saturated solutions:

saturated solution	$[K^+]_{tot}$	$[HC_4H_4O_6^-]$
I. no added KCl	$[K^+]_{tot} = [HC_4H_4O_6^-]$	determined by titration with NaOH
II. with added KCl	$[K^+]_{tot} = [HC_4H_4O_6^-] + [KCl]$	determined by titration with NaOH

In both cases the concentration of hydrogen tartrate ion is determined by titration. The calculated values of the K_{sp} should be the same in each case, but the lower solubility of potassium hydrogen tartrate in the second solution, due to the common ion effect of added KCl, will result in a lower concentration $[HC_4H_4O_6^-]$ found in the titration.

Making that comparison introduces another minor complication, the fact that chemical processes involving ions in solution can be affected merely by the presence of other charged species, whether or not they are directly involved in that process. The effect is related to the *activities* of the species, sometimes described as “effective concentrations”. Ions moving in an environment of other charged species with which they can interact behave slightly differently than when those other charges are absent. To make a fair comparison between the two different saturated solutions we will make sure that the one without extra potassium ions does at least have the same number of charged particles present, to keep the ionic environments more uniform.

REFERENCES:

1. Solubility of Potassium Bitartrate, James Madison University, Chemistry Department, <https://www.jmu.edu/chemistry/132%20Lab/Exp%209--Solubility%20of%20Potassium%20Bitartrate.pdf>, accessed 6 July 2017.
2. Solubility Product of Potassium Acid Tartrate, Los Angeles Mission College, http://www.profpaz.com/Files/chem102/Exp_13.pdf, accessed 6 July 2017.
3. The Common ion Effect and Solubility, David Dice, <http://www.digipac.ca/chemical/mtom/contents/chapter4/commonionlab.htm>, accessed 6 July 2017.
4. Solubilities of Potassium Hydrogen Tartrate and Potassium Chloride in Water + Ethanol Mixtures, P. Sousa and A.M.C. Lopes, *J. Chem. Eng. Data* **2001**, 46, 1362-1364.

PROCEDURE:

NOTE: The procedure as written has midshipmen working in pairs, with each pair working on the same saturated solution. Pairs would then exchange data with students using the other saturated solution. Your Instructor may prefer a different arrangement. Follow the guidance of your Instructor.

Titration of Saturated Potassium Hydrogen Tartrate Solution

1. Two midshipmen working together will need about 100 mL (*total*) of the appropriate saturated solution. Obtain about 100 mL of your assigned saturated solution of $\text{KHC}_4\text{H}_4\text{O}_6$ (Solution I or Solution II) in a clean, dry 100 mL beaker. Identify (circle) your assigned saturated solution on the Data page.
2. The saturated solution must be filtered before use; one filter set-up per pair of midshipmen is sufficient. Create a filter paper cone by folding a circle of filter paper in half, and then that semicircle in half again. Open the cone with three plies to one side and one on the other and insert it into a glass filter funnel. Set the funnel in a filter funnel rack, with a clean, dry 100 mL beaker below the spout.
3. Pour a small amount of the saturated solution into the filter paper cone, wetting it down to the glass funnel. Then continue to pour the solution through the filter, collecting the effluent. Use the filtered solution ONLY for all subsequent steps; there should be plenty for both midshipmen working together.
4. Rinse your 25 mL pipet with the filtered solution. (To rinse a pipet, draw up a small amount of liquid into the pipet and then manipulate the glassware so that the solution contacts all surfaces. *Discard* the rinse.)
5. Use a clean, dry 100 mL beaker to obtain ~ 100 mL of the standard NaOH solution. Record the concentration of the NaOH solution on the Data page. Label the beaker so it can be replenished if necessary without contamination of reagent.
6. ***Each*** midshipman in the pair should perform the following steps, so that each midshipman analyzes at least one sample of the saturated solution. There is sufficient equipment that each partner can do these steps at the same time. Record your data in the separate Trial 1 and Trial 2 columns for the appropriate saturated solution.
 - a. Using your rinsed pipet, transfer 25.00 mL of the filtered saturated solution into a 125 mL Erlenmeyer flask. Add about 20 mL of deionized water and 2 drops of phenolphthalein indicator solution. This is the sample of saturated potassium hydrogen tartrate you will analyze.
 - b. Use a small amount (~ 5 mL) of the NaOH solution to rinse your buret, coating all surfaces and discarding the rinse. Fill up the buret with the remaining NaOH solution and place it on a ring stand, using a buret clamp.
 - c. Set up the buret, ring stand and Erlenmeyer flask of sample. Place a piece of white paper under the Erlenmeyer flask.
 - d. Record the initial volume reading of the buret on the Data page. (Read the buret to *two* decimal places.)
 - e. Titrate the solution to the phenolphthalein end point, stirring or swirling as you go to ensure mixing. The end point is the first faint pink color that persists for at least 30 seconds. Record the final buret reading (to *two* decimal places) on the Data pages.
7. **If** the volumes of NaOH used for trials 1 and 2 do not agree within 1 mL, repeat step 6 (a-e) for a third trial. If you have good agreement, you may skip the third trial.
8. Obtain data from classmates assigned to work with the other saturated solution of $\text{KHC}_4\text{H}_4\text{O}_6$ (either Solution I or Solution II). Solution II data includes the concentration of KCl; be sure to record that as well. You need all data for two trials of each solution to do the analysis.

Clean-up

1. Empty all solutions down the drain, with flowing water. Discard any filter paper cones in the trash.
2. Clean, and then rinse all glassware with distilled water. Return materials to their original locations.

Name _____

Section _____

Partner _____

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DATA

Assigned saturated solution (circle)

Solution I**Solution II**

Concentration of NaOH solution: _____ M

Saturated Solution I KHC ₄ H ₄ O ₆		
Trial 1	Trial 2	Trial 3
25.00	25.00	25.00

Volume sample solution
(mL)Initial buret reading
(mL)Final buret reading
(mL)Volume NaOH
(mL)

Saturated Solution II KHC ₄ H ₄ O ₆ with added 0.015 M KCl		
Trial 1	Trial 2	Trial 3
25.00	25.00	25.00

DATA ANALYSIS

1. For each titration of each saturated solution, calculate the number of moles of OH⁻ used to reach the end point of the titration. Show your work for one of the trials for both Solution I and Solution II, and report the result for a second trial of each solution. (If you did three trials, only analyze the two that most closely agree.)

Solution I	Solution II
Results: First trial _____ mol OH ⁻ Second trial _____ mol OH ⁻	Results: First trial _____ mol OH ⁻ Second trial _____ mol OH ⁻

2. Using the stoichiometry of the titration reaction (reaction (3), p. E44-2) and the volume of the sample solution, calculate the molar concentration of $\text{HC}_4\text{H}_4\text{O}_6^-$ for each titration of each saturated solution. Show your work for one of the trials for both Solution I and Solution II, and report the result for a second trial of each solution. (If you did three trials, only analyze the two that most closely agree.)

Solution I	Solution II
Results: First trial _____ M $\text{HC}_4\text{H}_4\text{O}_6^-$ Second trial _____ M $\text{HC}_4\text{H}_4\text{O}_6^-$	Results: First trial _____ M $\text{HC}_4\text{H}_4\text{O}_6^-$ Second trial _____ M $\text{HC}_4\text{H}_4\text{O}_6^-$

3. Knowing the $[\text{HC}_4\text{H}_4\text{O}_6^-]$ in each solution, and the $[\text{KCl}]$ provided in saturated solution II, use the table on p. E44-2 to find the total potassium ion concentration $[\text{K}^+]_{\text{tot}}$ for each trial. Show your work for one of the trials for both Solution I and Solution II, and report the result for a second trial of each solution. (If you did three trials, only analyze the two that most closely agree.)

Solution I	Solution II
Results: First trial _____ M total K^+ Second trial _____ M total K^+	Results: First trial _____ M total K^+ Second trial _____ M total K^+

4. Use the measured $[\text{HC}_4\text{H}_4\text{O}_6^-]$ (question 2) and the calculated $[\text{K}^+]_{\text{tot}}$ (question 3) for each trial, calculate the K_{sp} for potassium hydrogen tartrate, $\text{KHC}_4\text{H}_4\text{O}_6$. Average the values obtained for the two trials of Solution I. Then average the values obtained for the two trials of Solution II. Show your work for one of the trials for both Solution I and Solution II, and report the result for a second trial of each solution. (If you did three trials, only analyze the two that most closely agree.)

Solution I	Solution II
Results: First trial _____ = K_{sp} Second trial _____ = K_{sp}	Results: First trial _____ = K_{sp} Second trial _____ = K_{sp}
Average K_{sp} without added KCl _____ = K_{sp} average	Average K_{sp} with added KCl _____ = K_{sp} average

5. Based on the measured $[\text{HC}_4\text{H}_4\text{O}_6^-]$ (question 2) and the molar mass of $\text{KHC}_4\text{H}_4\text{O}_6$, what is the gram solubility of $\text{KHC}_4\text{H}_4\text{O}_6$ in each of the solutions? Average the values obtained for the two trials of Solution I. Then average the values obtained for the two trials of Solution II. Show your work for one of the trials for both Solution I and Solution II, and report the result for a second trial of each solution. (*If you did three trials, only analyze the two that most closely agree.*)

Solution I	Solution II
Results: First trial _____ g/L $\text{KHC}_4\text{H}_4\text{O}_6$ Second trial _____ g/L $\text{KHC}_4\text{H}_4\text{O}_6$	Results: First trial _____ g/L $\text{KHC}_4\text{H}_4\text{O}_6$ Second trial _____ g/L $\text{KHC}_4\text{H}_4\text{O}_6$
Average solubility $\text{KHC}_4\text{H}_4\text{O}_6$ <i>without</i> added KCl _____ g/L avg. solubility	Average solubility $\text{KHC}_4\text{H}_4\text{O}_6$ <i>with</i> added KCl _____ g/L avg. solubility

Post-Lab Questions

1. Compare the values of K_{sp} determined for Solution I (without added KCl) and Solution II (with added KCl). Should they be the same, or different? Why? – Explain your answer.

2. Compare the values of the solubility determined for Solution I (without added KCl) and Solution II (with added KCl). Should they be the same, or different? Why? – Explain your answer.

3. At room temperature, the maximum solubility of KCl is 3.74 M, well above the KCl content of Solution II used in the experiment. Use the value of $K_{sp} = 1.1 \times 10^{-3}$ for $\text{KHC}_4\text{H}_4\text{O}_6$ and calculate what the solubility of $\text{KHC}_4\text{H}_4\text{O}_6$ would be in a solution which was also 3.74 M in KCl. Set up the I.C.E. table and show your work.

Name _____

Section _____

Date _____

Experiment 44**SOLUBILITY AND THE SOLUBILITY PRODUCT CONSTANT****Pre-Lab Exercises**

Complete this page prior to attending lab.

1. Write out the solubility equilibrium reactions, and K_{sp} expressions, for the following insoluble compounds. Be sure to include states of matter in your reactions.

a. AgCl

b. Ag_2SO_4

2. For Ag_2SO_4 the $K_{sp} = 1.2 \times 10^{-5}$ at $25^\circ C$. What is the solubility of Ag_2SO_4 in pure water? Show your work.

3. What will be the effects of the following changes applied to a saturated solution of Ag_2SO_4 ? For this substance, the enthalpy change associated with dissolving the salt ($\Delta_{\text{solution}}H$) is positive.

Circle the correct answers for each change of conditions.

Change of conditions	Effect on K_{sp}			Effect on solubility		
Increase temperature	increase	no change	decrease	increase	no change	decrease
Add Na_2SO_4 (s)	increase	no change	decrease	increase	no change	decrease
Add NaCl (s)	increase	no change	decrease	increase	no change	decrease
Add conc. HCl (aq) (Assume no volume change)	increase	no change	decrease	increase	no change	decrease