

# 1. The Solubility Product of Silver Acetate

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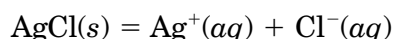
## Objective

The extent to which a sparingly soluble salt dissolves in water is frequently indicated in terms of the salt's solubility product equilibrium constant,  $K_{sp}$ . In this experiment,  $K_{sp}$  for the salt silver acetate will be determined, and the common ion effect will be demonstrated.

## Introduction

A previous experiment has discussed the concept of solubility. Solubility was defined to be the number of grams of a substance that will dissolve in 100 mL of solvent. For substances that dissolve to a reasonable extent in a solvent, the solubility is a useful method of describing how much solute is present in a solution. However, for substances that are only very sparingly soluble in a solvent, the solubility of the salt is not a very convenient means for describing a saturated solution. When the solute is only very sparingly soluble in the solvent, the solution is more conveniently (and correctly) described by the equilibrium constant for the dissolving process.

Consider the salt silver chloride, AgCl, which is very sparingly soluble in water. When a portion of solid silver chloride is placed in a quantity of pure water, Ag<sup>+</sup> ions and Cl<sup>-</sup> ions begin to dissolve from the crystals of solid and enter the water. As the number of Ag<sup>+</sup> and Cl<sup>-</sup> ions present in the water increases, the likelihood of the Ag<sup>+</sup> and Cl<sup>-</sup> ions reentering the solid increases. Eventually, an equilibrium is established between the solution and the undissolved solute crystals remaining: Ag<sup>+</sup> and Cl<sup>-</sup> ions will be dissolving from the crystals, while elsewhere Ag<sup>+</sup> and Cl<sup>-</sup> ions will "undissolve" at the same rate. Beyond this point, there will be no net increase in the number of Ag<sup>+</sup> and Cl<sup>-</sup> ions to be found in the solution at any future time. The solution has become **saturated**, which means that the ions that are dissolved have reached a state of equilibrium with the remaining undissolved solute.



In writing the equilibrium constant expression for this equilibrium, we might at first be tempted to write

$$K = [\text{Ag}^+(aq)][\text{Cl}^-(aq)]/[\text{AgCl}(s)]$$

in which square brackets [ ] refer as usual to concentrations in moles per liter. However, because AgCl(s) is a pure solid, its concentration is a *constant* value (a function of the density of the solid) and is included in the measured value of the equilibrium constant. For this reason, a new equilibrium constant,  $K_{sp}$ , called the **solubility product constant** is defined for the dissolving process outlined earlier:

$$K_{sp} = [\text{Ag}^+(aq)][\text{Cl}^-(aq)]$$

The fact that the concentration of the remaining undissolved solid AgCl does not enter into this equilibrium is easily observed experimentally because the measured value of the equilibrium constant is completely independent of the quantity of solid AgCl that remains. Whether there is one single crystal of undissolved AgCl remaining in contact with the saturated solution or 1000 g, the value of  $K_{sp}$  is a fixed number (varying only with temperature). The solubility product,  $K_{sp}$ , is generally preferred over the actual solubility (in g solute/100 mL solvent) because it is independent of a specific amount of solvent.

The solubility product,  $K_{sp}$ , is defined in terms of molar concentrations. However, the solubility in moles or grams per liter can be calculated from the solubility product. Suppose the solubility product for AgCl in pure water has been determined from experiment to be

$$K_{sp} = [\text{Ag}^+(aq)][\text{Cl}^-(aq)] = 1.6 \times 10^{-10}$$

If AgCl(s) has been dissolved in pure water, then

$$[\text{Ag}^+(aq)] = [\text{Cl}^-(aq)] = 1.3 \times 10^{-5} M$$

and  $1.3 \times 10^{-5}$  mol/L of AgCl(s) must have dissolved to produce these concentrations of the individual ions. The solubility of AgCl in grams per liter can then be simply calculated using the formula weight of AgCl(s).

In the preceding discussion, we considered the case in which the salt AgCl was dissolved in pure water. If we try to dissolve salt AgCl in a solution that already contains either  $\text{Ag}^+$  ion or  $\text{Cl}^-$  ion (from some other source), we will have to consider the effect that these already present ions will have on the dissolving of AgCl. Suppose again that  $K_{sp}$  for AgCl has been measured experimentally and was found to be given by

$$K_{sp} = [\text{Ag}^+(aq)][\text{Cl}^-(aq)] = 1.6 \times 10^{-10}$$

Suppose we try to dissolve AgCl(s) in a solution that contains 0.10 M  $\text{Cl}^-$  ion from another source (perhaps 0.10 M sodium chloride solution). On a microscopic basis, there is no distinction among  $\text{Cl}^-$  ions, whether they were produced by AgCl(s) dissolving or were provided from some other source. The solubility product equilibrium constant must be satisfied for AgCl(s) regardless of what else might be present in the solution. However, the  $[\text{Cl}^-(aq)]$  in the solution was already at the level of 0.10 M before AgCl(s) was added to the solution. Substituting this value into the expression for  $K_{sp}$ ,

$$K_{sp} = [\text{Ag}^+(aq)][0.10] = 1.6 \times 10^{-10}$$

gives us that the maximum concentration of  $\text{Ag}^+$  ion that can be present in the 0.10 M NaCl solution is

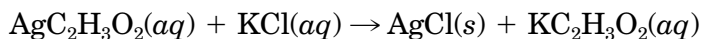
$$[\text{Ag}^+(aq)] = (1.6 \times 10^{-10})/0.10 = 1.6 \times 10^{-9} M$$

Since the only source of  $\text{Ag}^+$  ion is from the dissolving of AgCl(s), then  $1.6 \times 10^{-9}$  mol/L of AgCl(s) must have dissolved. This is approximately 10,000 times

less  $\text{AgCl}(s)$  than dissolved per liter of pure water. The presence of the common ion,  $\text{Cl}^-(aq)$ , already in the solvent has decreased the solubility of the sparingly soluble salt  $\text{AgCl}(s)$ .

In general, the presence of a common ion from another source will decrease the solubility of a sparingly soluble substance. The common ion effect is merely a demonstration of Le Châtelier's principle in action. If additional  $\text{Cl}^-(aq)$  is added to an equilibrium system involving  $\text{Cl}^-(aq)$ , then the equilibrium will shift so as to minimize the effect of the added  $\text{Cl}^-(aq)$ , resulting in a net decrease in the amount of  $\text{AgCl}(s)$  that can dissolve.

In this experiment, you will determine  $K_{sp}$  for the salt silver acetate. Silver acetate is not truly a "very sparingly soluble substance," but its concentration in a saturated solution is much less than for many common salts. However, because the solubility of silver acetate is appreciable, you may not get quite the agreement among results in this experiment that is usually expected.  $K_{sp}$  for silver acetate will be determined in water, in solutions in which a common ion is present, and in a solution in which ions that are not part of the solubility equilibrium are present. The concentration of silver ion in the silver acetate solutions will be determined by a precipitation titration of a standard potassium chloride solution (Mohr method), using potassium chromate as indicator. Silver acetate and potassium chloride react according to



From the volume of silver acetate solution required to titrate a given sample of standard KCl, the concentration of the silver acetate solution may be calculated by usual solution stoichiometric methods.

## SAFETY PRECAUTIONS

- **Wear safety glasses at all times while in the laboratory.**
- **Silver compounds can stain the skin if spilled. The stain is due to the reduction of silver ion to metallic silver on the skin and is not dangerous. The stain will wear off in 2–3 days.**
- **Chromium and nitrate compounds are toxic. Wash hands after use.**
- **Dispose of all reagents as directed by the instructor.**

## Apparatus/Reagents Required

10- and 25-mL pipets, buret and clamp, saturated silver acetate solution (in distilled water), saturated silver acetate solution (in 0.100 *M* potassium nitrate), saturated silver acetate solution (in 0.100 *M* silver nitrate), saturated silver acetate solution (in 0.100 *M* sodium acetate), 5% potassium chromate indicator, standard 0.0500 *M* potassium chloride

## Procedure

Record all data and observations directly in your notebook in ink.

Clean the 10- and 25-mL pipets and the buret by soaking with soap and water, followed by rinses with tap water and distilled water. Set up the buret in the buret clamp.

In order to be certain that the silver acetate solutions are saturated with silver acetate, an excess quantity of solid silver acetate has been added to each solution, which must be removed before the solutions are used in the titrations that follow.

### ***A. Determination of Silver Acetate in Distilled Water***

Obtain approximately 70 mL of saturated silver acetate (in distilled water) and filter through a gravity funnel/filter paper to remove any cloudiness/solid. Rinse the buret with small portions of the filtered silver acetate solution; then fill the buret and record the initial reading to the nearest 0.02 mL (reading the bottom of the meniscus).

Pipet 10 mL of the standard 0.0500 M KCl solution into a clean Erlenmeyer flask. Then add 15 mL of distilled water.

Add approximately 1 mL of 5% potassium chromate solution. The color change of this indicator is rather subtle, from bright lemon yellow to a “dirty” yellow/brown color.

Titrate the KCl solution with the silver acetate until the indicator changes color. Record the final volume of silver acetate solution in the buret.

Repeat the determination twice for consistent results.

From the concentration of the KCl and from the pipet and buret volumes, calculate the concentration, in moles per liter, of silver ion in the saturated solution of silver acetate in distilled water. Using the mean concentration of silver ion for your three determinations, calculate the solubility product of silver acetate.

### ***B. Determination of Silver Acetate in 0.100 M Potassium Nitrate***

Obtain approximately 70 mL of saturated silver acetate solution containing 0.100 M potassium nitrate. Potassium nitrate is an ionic substance, but is not involved in the solubility equilibrium of silver acetate. Filter the solution to remove cloudiness/solid. Rinse the buret with the filtered solution; then fill the buret and record the initial volume to the nearest 0.02 mL.

Pipet 10 mL of the standard 0.0500 M KCl solution into an Erlenmeyer flask. Add 1 mL of the 5% potassium chromate indicator.

Titrate the potassium chloride sample to the indicator endpoint, and record the final volume of silver acetate to the nearest 0.02 mL.

Repeat the determination twice for consistent results.

From the concentration of the standard potassium chloride solutions, and from the pipet and buret volumes, calculate the concentration of silver ions, in moles per liter, in the saturated silver acetate solution that also contains 0.100 *M* potassium nitrate. Using the mean concentration of silver ion, calculate the solubility product of silver acetate.

### ***C. Determination of Silver Acetate in 0.100 M Silver Nitrate***

Obtain approximately 70 mL of saturated silver acetate solution containing 0.100 *M* silver nitrate. Silver nitrate is an ionic solute that contains an ion common to the silver acetate solubility equilibrium. Filter the solution to remove cloudiness/solid. Rinse the buret with the filtered solution; then fill the buret and record the initial volume to the nearest 0.02 mL.

Pipet a 25-mL portion of the standard 0.0500 *M* KCl solution into an Erlenmeyer flask and add approximately 1 mL of the 5% potassium chromate solution.

Titrate the KCl sample with silver acetate solution until the indicator changes from lemon yellow to “dirty” yellow/brown.

Repeat the determination twice for consistent results.

From the concentration of the standard potassium chloride solution, and from the pipet and buret volumes, calculate the concentration of silver ion, in moles per liter, in the saturated silver acetate solution that also contains 0.100 *M* silver nitrate. Using the mean concentration of silver ion for your three determinations, calculate the solubility product of silver acetate.

### ***D. Determination of Silver Acetate in 0.100 M Sodium Acetate***

Obtain approximately 70 mL of saturated silver acetate solution containing 0.100 *M* sodium acetate. Sodium acetate is an ionic solute that contains an ion common to the silver acetate solubility equilibrium. Filter to remove cloudiness/solid. Rinse the buret with the filtered solution, and then fill the buret. Record the initial buret reading to the nearest 0.02 mL.

Pipet 10 mL of the standard 0.0500 *M* KCl solution into an Erlenmeyer flask, and add 15 mL of distilled water. Add approximately 1 mL of the 5% potassium chromate solution.

Titrate the KCl sample with the silver acetate solution to the indicator endpoint. Record the final volume of silver acetate to the nearest 0.02 mL.

Repeat the determination twice for consistent results.

From the concentration of the standard potassium chloride solution, and from the pipet and buret volumes, calculate the concentration of silver ion, in moles per liter, in the saturated silver acetate solution that also contains 0.100 *M* sodium acetate. Using the mean concentration of silver ion for your three determinations, calculate the solubility product for silver acetate.



# *The Solubility Product of Silver Acetate*

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Date: ..... Student name: .....  
Course: ..... Team members: .....  
Section: .....  
Instructor: .....

## **Prelaboratory Questions**

1. Write the specific definition of  $K_{sp}$  found in your textbook.
  
  
  
  
  
  
  
  
  
  
2. Using a handbook of chemical data, look up the values of  $K_{sp}$  for the following substances at 25°C:  
  
Silver chloride ..... Calcium carbonate .....  
Silver bromide ..... Silver acetate .....  
Barium sulfate ..... Calcium hydroxide .....
  
3. The solubility product of lead chromate is  $2.0 \times 10^{-16}$ . Calculate the solubility in moles per liter of lead chromate in each of the following solutions:
  - a. Saturated lead chromate in water
  
  
  
  
  
  
  
  
  
  
  - b. Saturated lead chromate in 0.10 M  $\text{Na}_2\text{CrO}_4$  solution
  
  
  
  
  
  
  
  
  
  
  - c. Saturated lead chromate in 0.001 M  $\text{Pb}(\text{NO}_3)_2$  solution



# The Solubility Product of Silver Acetate

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Date: ..... Student name: .....  
Course: ..... Team members: .....  
Section: .....  
Instructor: .....

## Results/Observations

### A. Silver Acetate/Water

mL standard KCl taken .....

Titration volumes	Sample 1	Sample 2	Sample 3
Initial volume AgAc	.....	.....	.....
Final volume AgAc	.....	.....	.....
Volume AgAc used	.....	.....	.....
Molarity of Ag <sup>+</sup> ion	.....	.....	.....

Mean molarity of Ag<sup>+</sup> ion .....

$K_{sp}$  for silver acetate.....

### B. Silver Acetate/Potassium Nitrate

mL standard KCl taken .....

Titration volumes	Sample 1	Sample 2	Sample 3
Initial volume AgAc	.....	.....	.....
Final volume AgAc	.....	.....	.....
Volume AgAc used	.....	.....	.....
Molarity of Ag <sup>+</sup> ion	.....	.....	.....

Mean molarity of Ag<sup>+</sup> ion .....

$K_{sp}$  for silver acetate.....

### C. Silver Acetate/Silver Nitrate

mL standard KCl taken .....

Titration volumes	Sample 1	Sample 2	Sample 3
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Initial volume AgAc	.....	.....	.....
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Final volume AgAc	.....	.....	.....
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Volume AgAc used	.....	.....	.....
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Molarity of Ag <sup>+</sup> ion	.....	.....	.....
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Mean molarity of Ag<sup>+</sup> ion .....

$K_{sp}$  for silver acetate.....

### D. Silver Acetate/Sodium Acetate

mL standard KCl taken .....

Titration volumes	Sample 1	Sample 2	Sample 3
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Initial volume AgAc	.....	.....	.....
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Final volume AgAc	.....	.....	.....
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Volume AgAc used	.....	.....	.....
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Molarity of Ag <sup>+</sup> ion	.....	.....	.....
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Mean molarity of Ag<sup>+</sup> ion .....

$K_{sp}$  for silver acetate.....

Based on Parts A, B, C, and D, calculate a mean value and the standard deviation for  $K_{sp}$  for silver acetate.

Student name: ..... Course/Section: ..... Date: .....

## Questions

1. In theory, the solubility product equilibrium constant should be, in fact, constant throughout your four sets of determinations. What factors may not have been considered that might have led to different measured values for  $K_{sp}$  under the various conditions used in the experiment?
2. Compare your mean  $K_{sp}$  value with the literature value. Calculate the percent error.
3. How does  $K_{sp}$  vary with temperature?

