Solubility Product Constant, $K_{sp}$

Equipment
- 2-25.00 mL burette
- 2-250 mL beakers
- 0.300 M $\text{NaC}_2\text{H}_3\text{O}_2$
- 0.200 M $\text{AgNO}_3$
- ferric alum indicator
- 0.100 M $\text{KCN}$

Objectives.
The objective of this experiment is to illustrate the use the Solubility Product Constant and determine the $K_{sp}$ value for silver acetate.

Background
In general, when ionic compounds dissolve in water, they go into solution as ions. When the solution becomes saturated with ions, that is, unable to hold any more, the excess solid settles to the bottom of the container and an equilibrium is established between the undissolved solid and the dissolved ions.

For example, when enough calcium oxalate is introduced into solution for it to become saturated, the following equilibrium is established.

$$\text{CaC}_2\text{O}_4(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{C}_2\text{O}_4^{2-}(aq)$$

If we write an equilibrium expression for this situation, we obtain:

$$K_{sp} = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}]$$

Note that the solid itself does not appear as a denominator in the expression since it is a it is not in the same phase as the aqueous ions.

In general, the **solubility product constant** ($K_{sp}$), is the equilibrium constant for the solubility equilibrium of a slightly soluble ionic compound.

Like all equilibrium constants, the $K_{sp}$ is temperature dependent, but at a given temperature it remains relatively constant.

It also noteworthy, that, just like any equilibrium expression, each ion concentration in the expression is raised to the power of its coefficient in the solubility equation.

**For example**, the $K_{sp}$ expression for

$$\text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq)$$

is

$$K_{sp} = [\text{Ca}^{2+}][\text{CO}_3^{2-}]$$

but for the equation

$$\text{PbI}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2 \text{I}^{-}(aq)$$

$$K_{sp} = [\text{Pb}^{2+}][\text{I}^{-}]^2$$

note that the concentration of the iodide ion is squared.
Safety Precautions

Safety goggles must be worn in the lab at all times. Any skin contacted by chemicals should be washed immediately.

Procedure

**Preparation of a Saturated Silver Acetate Solution**

*Remember that this is a quantitative experiment. All measurements are to be made carefully, clean apparatus is to be used, material is to be handled to avoid loss, and standard solutions are to be added to clean dry burettes.*

The solubility of silver acetate is described by the equilibrium;

\[
\text{AgC}_2\text{H}_3\text{O}_2(s) \rightleftharpoons \text{Ag}^{+1}(aq) + \text{C}_2\text{H}_3\text{O}_2^{-1}(aq)
\]

The equilibrium expression defining this reaction is

\[
K_{sp} = [\text{Ag}^{+1}][\text{C}_2\text{H}_3\text{O}_2^{-1}]
\]

In order to determine this \(K_{sp}\), we must measure the silver ion and acetate ion concentrations in a saturated solution. Note, that their concentrations do not necessarily have to be equal...it is only the product of their concentrations that cannot exceed the \(K_{sp}\).

First we must create a saturated solution of silver acetate. Prepare one of the following (1-3) saturated solutions:

**Solution 1:** Add 20.0 ml of 0.200 M \(\text{AgNO}_3\) to 30.0 ml of 0.300 M \(\text{NaC}_2\text{H}_3\text{O}_2\).

**Solution 2:** Add 25.0 ml of 0.200 M \(\text{AgNO}_3\) to 25.0 ml of 0.300 M \(\text{NaC}_2\text{H}_3\text{O}_2\).

**Solution 3:** Add 30.0 ml of 0.200 M \(\text{AgNO}_3\) to 20.0 ml of 0.300 M \(\text{NaC}_2\text{H}_3\text{O}_2\).

The solutions of silver nitrate and sodium acetate separately have higher concentrations of \(\text{Ag}^{+1}\) and \(\text{C}_2\text{H}_3\text{O}_2^{-1}\) ions than can exist together in a single solution. Consequently, silver acetate precipitates until the *quantities defined by the solubility product constant are reached*.

If we **determine the amount of silver still left in solution**, we can use a little stoichiometry to determine how much acetate is left.

Stir and shake the solution to induce precipitation. Continue to stir intermittently for 30 minutes to bring about equilibrium between solid and dissolved silver acetate. Filter the solution through dry filter paper and funnel into a dry container. The filtrate should be a saturated solution with respect to \(\text{Ag}^{+1}\) and \(\text{C}_2\text{H}_3\text{O}_2^{-1}\) ions.

In order to calculate \(K_{sp}\), the concentration of \(\text{Ag}^{+1}\) ions is to be determined by titration with standard 0.100 M potassium thiocyanate solution, \(KCNS\). This titration forms insoluble silver thiocyanate.

\[
\text{Ag}^{+1}(aq) + \text{CNS}^{-1}(aq) \rightleftharpoons \text{AgCNS}(s)
\]
The endpoint of the titration is determined with Fe$^{3+}$ ions (supplied by ferric alum). Fe$^{3+}$ ions react with excess CNS$^{-1}$ ions to give a bright red color.

\[
\text{Fe}^{3+} + 3 \text{CNS}^{-1} \rightarrow \text{Fe(CNS)}^{(\text{red})}
\]

However, so long as Ag$^{+1}$ ions are present, CNS$^{-1}$ ions cannot accumulate to the point where the red color is permanent. As soon as the precipitation of AgCNS is complete, one drop of the thiocyanate solution forms a permanent light red color. This is the endpoint of the titration.

**Titration of Ag$^{+1}$**

1. Record the volumes of AgNO$_3$ and NaC$_2$H$_3$O$_2$ used to prepare your saturated silver acetate solution on your Report Sheet. Also record the total volume of the mixture. (1-3)

2. **Calculate the initial moles of Ag$^{+1}$ and C$_2$H$_3$O$_2^{-1}$** present in the solution. (4-5)

3. Assemble two clean, dry burettes. Rinse the burettes with small portions of the solutions which are to be placed in each (this technique is necessary to avoid diluting the solutions).

4. Fill one burette with standard 0.100 M potassium thiocyanate and place your saturated silver acetate solution in the other.

5. Draw into a clean 250-ml beaker or Erlemeyer flask 10.00-ml of the solution from the silver acetate burette, measuring its volume as accurately as you can (estimate between divisions) and **record this volume on your Report Sheet** (6).

6. Add 1 ml of the indicator (saturated ferric alum in 1M HNO$_3$). If the solution is red, add a few drops of concentrated HNO$_3$ until the solution pales.

7. Run a few drops of thiocyanate solution into the aliquot of silver acetate. Notice that a red color forms but disappears on stirring. Continue to add the thiocyanate solution, a drop at a time, until one drop gives a permanent light red color. **Record the amount of thiocyanate solution added on your Report Sheet.** (7)

8. Calculate from your titration data the number of moles of silver ion (Ag$^{+1}$) in in the 10.00 mL portion of your silver acetate solution and **record this on your Report Sheet.** (8)

9. Using the result from step 8., calculate the moles of silver in the entire 50.00 mL silver acetate solution. (9) **Convert this to moles per liter** and record this value on your Report Sheet. (10)

10. Given that we know the initial moles of Ag$^{+1}$ used to prepare the saturated solution (4) and the number of moles still in solution (9), we can **calculate the number of moles of Ag$^{+1}$ that must have precipitated.** (11) **Record this value on your Report Sheet.**

11. Since the silver and acetate are in a 1:1 proportion in the compound, **the number of moles of acetate precipitated must equal the number of moles of silver precipitated** (11) **Record the moles of acetate precipitated on your Report Sheet.** (12)
12. Given the initial moles of acetate used to prepare our saturated solution (5) and the number of moles of acetate precipitated (12), **calculate the number of moles of acetate remaining in solution and record this value on your Report Sheet.** (13)

13. Using the moles of acetate remaining in solution and the total volume of the solution, calculate the Molarity of acetate ion and **record this value on your Report Sheet.** (14)

14. Now that we have the Molarity of the Ag$^{+1}$ ion remaining in solution (10) and the Molarity of the C$_2$H$_3$O$_2^{-1}$ ion remaining in solution (14), we can calculate the $K_{sp}$ for AgC$_2$H$_3$O$_2$. **Record this value on your Report Sheet.** (15)

15. Given that the solubility of Silver Acetate is 10.2 g/L, calculate the accepted value for the $K_{sp}$ of AgC$_2$H$_3$O$_2$ and **record this value on your Report Sheet.** (16)

16. Calculate your % error for each of the two trials using the accepted value determined in the previous step and **record this value on your Report Sheet.** (17)
REPORT SHEET
Solubility Product Constant, $K_{sp}$

<table>
<thead>
<tr>
<th></th>
<th>Solution #1</th>
<th>Solution #2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. mL AgNO$_3$ (0.200 M)</td>
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</tr>
<tr>
<td>2. mL NaC$_2$H$_3$O$_2$ (0.300 M)</td>
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<tr>
<td>3. Volume of mixture (mL)</td>
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<tr>
<td>4. Moles of Ag$^{+1}$ initially present</td>
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<tr>
<td>5. Moles of C$_2$H$_3$O$_2^{-1}$ initially present</td>
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<tr>
<td>6. mL AgC$_2$H$_3$O$_2$ used in the titration</td>
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<tr>
<td>7. mL 0.100 M KCNS required for titration</td>
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<tr>
<td>8. Moles Ag$^{+1}$ in aliquot</td>
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<tr>
<td>9. Moles Ag$^{+1}$ in original 50.0 mL sample</td>
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<tr>
<td>10. Moles per liter of Ag$^{+1}$</td>
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<tr>
<td>11. Moles Ag$^{+1}$ precipitated</td>
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<tr>
<td>12. Moles C$_2$H$_3$O$_2^{-1}$ precipitated</td>
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<tr>
<td>13. Moles C$_2$H$_3$O$_2^{-1}$ remaining in solution</td>
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<tr>
<td>14. Moles per liter of C$_2$H$_3$O$_2^{-1}$</td>
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<tr>
<td>15. $K_{sp}$ for AgC$_2$H$_3$O$_2$</td>
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<tr>
<td>16. Accepted $K_{sp}$</td>
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<tr>
<td>17. Percent error</td>
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</tbody>
</table>

Show all calculations:
Questions

1. The $K_{sp}$ for calcium oxalate, $\text{CaC}_2\text{O}_4$, at 25°C is $1.8 \times 10^{-9}$. Calculate its solubility in g/L.

2. The solubility of $\text{PbCl}_2$ at 25°C is 0.990 g/100 mL. Calculate its $K_{sp}$.

3. If 500 mL of 0.010 M $\text{Pb(NO}_3)_2$ are added to 500 mL of a 0.010 M HCl solution, will a precipitate of $\text{PbCl}_2$ form? Explain.
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CHEMISTRY 132  
Name: ________________________
Laboratory Section ________

PRELAB: Exp. 5  
Solubility Product Constant, $K_{sp}$.

1. Write the $K_{sp}$ expression for the following compounds.
   
a) $\text{Mn}_3(\text{PO}_4)_2$

   b) $\text{Ag}_2\text{CrO}_4$

2. Given that the solubility of $\text{SrF}_2$ is $4.5 \times 10^{-5}$ g/L, calculate its $K_{sp}$.

3. If 2.00 mL of 0.1 M NaOH is added to 1.0 L of 0.100 M $\text{CaCl}_2$, will precipitation occur? Explain. ($K_{sp}$ for $\text{Ca(OH)}_2 = 5.4 \times 10^{-6}$)

4. The $K_{sp}$ for manganese(II)carbonate, $\text{MnCO}_3$, is $1.8 \times 10^{-11}$. Calculate its solubility in g/L.

5. What is the pH of a saturated $\text{Zn(OH)}_2$ solution given that the $K_{sp}$ for zinc hydroxide is $1.8 \times 10^{-14}$.