Unit 3: Solubility Equilibrium
Topic C: Quantitative Aspects of Solubility Equilibrium

In this topic we will examine:

- how to apply the equilibrium law to solubility equilibria
- how to compute values of \( K_{sp} \) from ion concentrations
- how to compute solubility from \( K_{sp} \)
- how to calculate the maximum ion concentration in a solution
- how to use the \( K_{sp} \) to predict if a precipitate will form when solutions are mixed
- the theory and practice of solubility titrations

C.1: Introduction to the \( K_{sp} \)

The Equilibrium Law studied in Unit 2 applies to systems of solubility equilibrium (and all other equilibrium systems) with only slight modifications.

Consider the equilibrium:

\[ \text{BaSO}_4(\text{s}) \rightleftharpoons \text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \]

Following the rules for writing equilibrium constant expressions discussed in Unit 2, the \( K_{eq} \) expression for this equilibrium is:

\[ K_{eq} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] \]

Because the concentration of the solid \( \text{BaSO}_4 \) does not change, it does not appear in the equilibrium expression.

To indicate that an equilibrium constant is for a solubility equilibrium system, we give it a different name and use a slightly different symbol to represent it.

\[ K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] \]

The subscript "sp" denotes "solubility product", and equilibrium constant expressions written for solubility equilibria are usually called "solubility product constant expressions" or "\( K_{sp} \) expressions".

Some texts refer to \( K_{sp} \) expressions and "ion product constant" expressions. This name comes from the idea that we simply multiply the equilibrium concentrations of the product ions to obtain the value of the \( K_{sp} \) for a solubility equilibrium system. Such an idea is inaccurate and misleading. Consider the following equilibrium:

\[ \text{Ca(IO}_3)_2(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + 2\text{IO}_3^{-}(\text{aq}) \]

According to the rules for writing equilibrium constant expressions, the correct \( K_{sp} \) expression is:

\[ K_{sp} = [\text{Ca}^{2+}][\text{IO}_3^{-}]^2 \]
Obviously, this is more than a simple product of the ion concentrations. The $K_{sp}$ of a system in a state of solubility equilibrium has all the same important characteristics of any other equilibrium constant:

- $K_{sp}$ values are affected only by changes in temperature
- a large $K_{sp}$ value indicates that products are favoured at equilibrium (i.e., ion concentrations are large at equilibrium), and
- a small $K_{sp}$ value indicates that reactants are favoured at equilibrium (i.e., ion concentrations are small at equilibrium).

The last two points above lead to the following **general** conclusion:

| The greater the $K_{sp}$ value, the greater the solubility of the salt. |

The above conclusion is very general. As we will see, when asked to compare the solubility of two salts, it is often not simply a matter of comparing their $K_{sp}$ values. We must also consider the mole ratios in their respective dissociation equations.

Nearly all $K_{sp}$ values that we will deal with in this topic are very small ($10^{-5}$ to $10^{-39}$). On page 5 of the Chemistry 12 Data Booklet is a table of Solubility Product Constants at $25^\circ$C. Throughout this topic, you may need to refer to this table for required $K_{sp}$ values.

**Examples:**

Write the solubility equilibrium equation and the $K_{sp}$ expressions for saturated solutions of each of the following salts.

- a) $\text{AgCl}_(s)$
- b) $\text{Mg(OH)}_2(s)$
- c) $\text{Ca}_3(\text{PO}_4)_2(s)$
Provincial Exam Examples: K\textsubscript{sp} Expressions

1. For a saturated solution, the K\textsubscript{sp} expression does not contain any solid solute term. What is the reason for this?

A. The solid solute is a product.
B. The solid solute is a reactant.
C. The solid solute continues to change in amount.
D. The solid solute does not change in concentration.

2. The K\textsubscript{sp} expression for a saturated solution of Ba\textsubscript{3}(AsO\textsubscript{4})\textsubscript{2} is

A. K\textsubscript{sp} = [Ba\textsuperscript{2+}][AsO\textsubscript{4}\textsuperscript{3-}]
B. K\textsubscript{sp} = [Ba\textsuperscript{2+}]	extsuperscript{3}[AsO\textsubscript{4}\textsuperscript{3-}]	extsuperscript{2}
C. K\textsubscript{sp} = [3Ba\textsuperscript{2+}][2AsO\textsubscript{4}\textsuperscript{3-}]
D. K\textsubscript{sp} = [3Ba\textsuperscript{2+}]	extsuperscript{3}[2AsO\textsubscript{4}\textsuperscript{3-}]	extsuperscript{2}

3. Given the equilibrium reaction:

\[ 2\text{NaNO}_3(aq) + \text{Ag}_2\text{S(s)} \rightleftharpoons 2\text{AgNO}_3(aq) + \text{Na}_2\text{S(aq)} \]

Which K\textsubscript{sp} expression best describes the net ionic reaction?

A. K\textsubscript{sp} = [Ag\textsuperscript{+}]\textsuperscript{2}[S\textsuperscript{2-}]
B. K\textsubscript{sp} = \frac{[Ag\textsuperscript{+}]\textsuperscript{2}[S\textsuperscript{2-}]}{[Ag_2S]}
C. K\textsubscript{sp} = \frac{1}{[Ag\textsuperscript{+}]\textsuperscript{2}[S\textsuperscript{2-}]}
D. K\textsubscript{sp} = \frac{[AgNO_3]^2[Na_2S]}{[NaNO_3]^2}

4. Which of the following expressions represents [Fe\textsuperscript{3+}] in a saturated Fe(OH)\textsubscript{3} solution?

A. \frac{K\textsubscript{sp}}{3[OH^-]}
B. \frac{K\textsubscript{sp}}{[OH^-]^3}
C. \sqrt[3]{\frac{K\textsubscript{sp}}{[OH^-]}}
D. K\textsubscript{sp} \times [OH^-]\textsuperscript{3}

Hebden Reference: Sections III.6

Practice Exercises:

Complete the following exercises from the Hebden text:

Page 91 Exercise 40.
C.2: Calculations Involving the K$_{sp}$

We can perform a number of different types of computations that involve the K$_{sp}$ of solubility equilibria systems. Many of these calculations are similar to the five different types of K$_{eq}$ calculations performed in Unit 2.

C.2.1 Calculating K$_{sp}$ Values From the Solubility of a Salt

In Unit 2, we calculated K$_{eq}$ values given the equilibrium concentrations of all involved substances.

A similar type of calculation for solubility equilibria requires us to calculate the K$_{sp}$ value for a salt from its concentration, given either in units of mol/L (or M) or g/L. If the solubility of a salt is given in units of g/L, we MUST convert it to units of mol/L (or M) before we can calculate a K$_{sp}$ value.

Thus, two skills learned in Topic A of this unit will need to be used. Firstly, we need to be able to determine the molar concentration of each ion present at equilibrium using the solubility and the mole ratio, and, on occasion, be able to convert units of g/L to mol/L.

When calculating a K$_{sp}$ value from the solubility of a salt, it is advised that one ALWAYS write out the equilibrium reaction equation as an initial step. This will remind us that the mole ratio must be used.

Example:

The solubility of copper (II) hydroxide at 25°C is 3.40 x 10$^{-7}$ mol/L. Determine the K$_{sp}$ for this salt at this temperature.

Solution:

Start by writing out the equilibrium reaction equation:

$$\text{Cu(OH)}_2(\text{s}) \rightleftharpoons \text{Cu}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq})$$

The 1:1:2 mole ratio tells us that the equilibrium concentrations of the two ions are:

Equilibrium [Cu$^{2+}$] = 3.40 x 10$^{-7}$ M, equilibrium [OH$^-$] = 6.80 x 10$^{-7}$ M

The K$_{sp}$ expression for the equilibrium is:

$$K_{sp} = [\text{Cu}^{2+}][\text{OH}^-]^2$$

Inserting the equilibrium concentrations of each ion into this expression we get:

$$K_{sp}(\text{Cu(OH)}_2) = (3.40 \times 10^{-7})(6.80 \times 10^{-7})^2$$

$$= 1.57 \times 10^{-19}$$
Practice:

1. Calculate the $K_{sp}$ of each of the following salts from its stated solubility at 25°C.

   a) $\text{Ag}_2\text{CO}_3$; solubility = $1.16 \times 10^{-4}$ mol/L

   b) $\text{Fe(OH)}_2$; solubility = $1.5 \times 10^{-3}$ g/L

   c) $\text{Mg}_3(\text{PO}_4)_2$; solubility = $7.2 \times 10^{-6}$ g/L

2. A 100.0 mL sample of a saturated $\text{CaF}_2$ solution was heated to dryness. It was determined that the sample contained $2.15 \times 10^{-5}$ moles of the solid. Using this information, calculate the $K_{sp}$ value for $\text{CaF}_2$. 
Provincial Exam Examples: Calculating $K_{sp}$ From Given Solubility

1. The solubility of ZnCO$_3$ is $6.4 \times 10^{-9}$ M. What is the $K_{sp}$ for ZnCO$_3$?
   
   A. $4.1 \times 10^{-17}$  
   B. $6.4 \times 10^{-9}$  
   C. $1.3 \times 10^{-8}$  
   D. $8.0 \times 10^{-5}$

2. The solubility of Mg(OH)$_2$ is found to be $1.2 \times 10^{-4}$ M. What is its $K_{sp}$?
   
   A. $6.9 \times 10^{-12}$  
   B. $1.7 \times 10^{-12}$  
   C. $1.4 \times 10^{-8}$  
   D. $1.2 \times 10^{-4}$

3. The solubility of NiCO$_3$ is $4.4 \times 10^{-2}$ g/L. Determine the $K_{sp}$ value for NiCO$_3$.
   
   A. $1.4 \times 10^{-7}$  
   B. $3.7 \times 10^{-4}$  
   C. $1.9 \times 10^{-3}$  
   D. $2.1 \times 10^{-1}$

4. Which of the following describes the relationship between the solubility product constant ($K_{sp}$) and the solubility ($s$) of PbI$_2$?
   
   A. $K_{sp} = s^2$  
   B. $K_{sp} = 4s^3$  
   C. $s = \sqrt[3]{\frac{K_{sp}}{4}}$  
   D. $s = \sqrt[3]{K_{sp}}$

5. After drying a 50.0 mL sample of a saturated solution of Ag$_2$SO$_4$ was heated to dryness, $7.2 \times 10^{-4}$ g of solid Ag$_2$SO$_4$ remained. What is the value of $K_{sp}$ for Ag$_2$SO$_4$?
C.2.2: Calculating Solubility From the $K_{sp}$ Value

Firstly, it is important to realize that **A SALT'S SOLUBILITY AND ITS $K_{sp}$ VALUE ARE NOT THE SAME THING**.

Calculating the solubility of a salt from its $K_{sp}$ value is similar to the type of calculation performed in Unit 2 where we are asked to calculate one or more equilibrium concentrations given the initial concentrations of all species and the $K_{eq}$ value.

Just as that type of Unit 2 calculation, use of an ICE table is strongly recommended. As well, determining the solubility of a salt from its $K_{sp}$ value requires that we represent an unknown concentration change with the variable "$x$".

**Example:**

1. Calculate the molar solubility of AgBrO$_3$ if it has a $K_{sp} = 5.77 \times 10^{-15}$.

**Solution:**

Begin by writing out the solubility equilibrium equation for a saturated solution of AgBrO$_3$ and creating an ICE table.

<table>
<thead>
<tr>
<th>[Initial] (before any AgBrO$_3$ dissolves)</th>
<th>AgBrO$<em>3$$</em>{(s)}$</th>
<th>$=$</th>
<th>$\text{Ag}^+_{(aq)}$</th>
<th>+</th>
<th>$\text{BrO}<em>3^-</em>{(aq)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Change in] when $x$ mol/L of AgBrO$_3$</td>
<td>not applicable</td>
<td>0 M</td>
<td>not applicable</td>
<td>+ $x$</td>
<td>+ $x$</td>
</tr>
<tr>
<td>[Equilibrium]</td>
<td>not applicable</td>
<td>$x$</td>
<td>$x$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In the table above, $x$ represents the molar solubility of AgBrO$_3$. Because of the 1:1:1 mole ratio, when $x$ mol/L of the salt dissolves and dissociates, $x$ mol/L of each of the two ions is produced.

The $K_{sp}$ expression is:

$$K_{sp} = [\text{Ag}^+][\text{BrO}_3^-] = 5.77 \times 10^{-15}$$

Substituting and solving, we get:

$$K_{sp} = (x)(x) = 5.77 \times 10^{-15}$$

$$x^2 = 5.77 \times 10^{-15}$$

Taking the square root of both sides,

$$x = 7.596051606 \times 10^{-8}$$
Thus, the solubility of AgBrO$_3$ is $7.60 \times 10^{-8}$ M. Notice that, because of the simple mole ratio, the equilibrium concentration of both ions at equilibrium is also $7.60 \times 10^{-8}$ M.

2. Calculate the concentration of OH$^-$ ions in a saturated solution of Mg(OH)$_2$.

**Solution:**

This example is complicated by three factors:

a) We are not provided with the K$_{sp}$ of Mg(OH)$_2$.

The required K$_{sp}$ value may be located on the table of Solubility Product Constants on page 5 of the Data Booklet.

$$K_{sp}(\text{Mg(OH)}_2) = 5.6 \times 10^{-12}$$

Note: the use of this value means we are assuming that $T = 25^\circ$C.

b) We are not actually asked to determine the molar solubility of Mg(OH)$_2$. Rather, we are asked to calculate the equilibrium [OH$^-$]. To determine this, we need to find the molar solubility of Mg(OH)$_2$ first, then the equilibrium [OH$^-$].

c) Mg(OH)$_2$ does not dissociate with a 1:1:1 mole ratio. This will complicate the mathematics of the problem somewhat.

Start by writing the equilibrium reaction equation and building an ICE table as before.

\[
\begin{array}{|c|c|c|c|}
\hline
& \text{Mg(OH)}_2(\text{s}) & = & \text{Mg}^{2+}(\text{aq}) + 2\text{OH}^- (\text{aq}) \\
\text{Initial} & \text{not applicable} & 0 \text{ M} & 0 \text{ M} \\
\text{Change in} & \text{not applicable} & + x & + 2x \\
\text{Equilibrium} & \text{not applicable} & & \\
\hline
\end{array}
\]

The K$_{sp}$ expression is:

$$K_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2$$

Substituting and solving we get:

Finally, since the equilibrium [OH$^-$] = 2x, the equilibrium [OH$^-$] = ________________
3. Calculate the solubility of SrF$_2$ at 25°C in units of g/L.

4. Determine the mass of solid SrSO$_4$ dissolved in 2.50 L of a saturated solution at 25°C.

**C.2.2.1: Using $K_{sp}$ values to Compare the Solubility of Salts**

Let us suppose you were asked to determine which of two salts has the greater molar solubility given their $K_{sp}$ values.

One way to determine which salt has the greater solubility is to go ahead and calculate the solubility of each from its $K_{sp}$ value and compare the results. However, there is an easier method.

Previously, it was stated that in general, the solubility of a substance is reflected by its $K_{sp}$ value (small $K_{sp}$ = low solubility, big $K_{sp}$ = high solubility). However, we cannot always predict which of two given salts has the larger solubility based solely on examination of their $K_{sp}$ values. One must also take into consideration the mole ratios with which each dissociates.

Consider the following salts and their $K_{sp}$ values at 25°C:

- $\text{BaCO}_3$ \[ K_{sp} = 2.6 \times 10^{-9} \]
- $\text{CuI}$ \[ K_{sp} = 1.3 \times 10^{-12} \]
- $\text{SrS}$ \[ K_{sp} = 3.4 \times 10^{-7} \]

Each of these salts dissociates with a 1:1:1 mole ratio:
\[
\begin{align*}
\text{BaCO_3(s)} & \rightleftharpoons \text{Ba}^{2+} \text{(aq)} + \text{CO}_3^{2-} \text{(aq)} \\
\text{CuI(s)} & \rightleftharpoons \text{Cu}^{+} \text{(aq)} + \text{I}^{-} \text{(aq)} \\
\text{SrS(s)} & \rightleftharpoons \text{Sr}^{2+} \text{(aq)} + \text{S}^{2-} \text{(aq)}
\end{align*}
\]

From our previous work, we know that the molar solubility of each of these salts is equal to the square root of its \(K_{sp}\) value (see Example 1 on pages 8 and 9 of this handout). That is:

\[
\text{solubility} = \sqrt{K_{sp}}
\]

For salts dissociating with a 1:1:1 mole ratio.

This being the case, of the three salts listed above, the one with the smallest \(K_{sp}\) (CuI in this case) will have the lowest molar solubility as well.

Now consider the following three salts and their \(K_{sp}\) values at 25°C:

\[
\begin{align*}
\text{Cu(IO}_3\text{)}_2 & \quad K_{sp} = 6.9 \times 10^{-8} \\
\text{Fe(OH)}_2 & \quad K_{sp} = 4.9 \times 10^{-17} \\
\text{Ag}_2\text{CrO}_4 & \quad K_{sp} = 1.1 \times 10^{-12}
\end{align*}
\]

These salts dissociate with either a 1:1:2 or a 1:2:1 mole ratio.

\[
\begin{align*}
\text{Cu(IO}_3\text{)}_2(s) & \rightleftharpoons \text{Cu}^{2+} \text{(aq)} + 2\text{IO}_3^{-} \text{(aq)} \\
\text{Fe(OH)}_2(s) & \rightleftharpoons \text{Fe}^{2+} \text{(aq)} + 2\text{OH}^{-} \text{(aq)} \\
\text{Ag}_2\text{CrO}_4(s) & \rightleftharpoons 2\text{Ag}^{+} \text{(aq)} + \text{CrO}_4^{2-} \text{(aq)}
\end{align*}
\]

From our previous work, we know that the molar solubility of each of these salts is equal to the cube root of one-fourth of its \(K_{sp}\) value. That is:

\[
\text{solubility} = \sqrt[3]{\frac{K_{sp}}{4}}
\]

This being the case, the salt having the lowest \(K_{sp}\) (Fe(OH)_2 in this case) will have the lowest molar solubility. Furthermore, we can draw the following conclusion that _________________ has the highest solubility of the three salts.

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**When comparing \(K_{sp}\) values for salts that dissociate with congruent mole ratios, the salt having the smallest \(K_{sp}\) value will also have the lowest molar solubility.**

If you need further evidence of the importance of the mole ratios, use the \(K_{sp}\) values for lead (II) iodate and silver bromide to calculate the molar solubility of each. You will see that the compound with the higher \(K_{sp}\) has the lower molar solubility!
Provincial Exam Examples: Calculating Solubility From $K_{sp}$ Values and Using $K_{sp}$ Values to Compare the Solubility of Salts

1. Which of the following is true for the salt SrF$_2$ at 25°C?

A. It has a high solubility.
B. It will not dissolve at all.
C. Its solubility is $1.6 \times 10^{-3}$ M.
D. Its solubility is $1.0 \times 10^{-3}$ M.

2. Calculate the solubility of PbSO$_4$.

A. $3.2 \times 10^{-16}$ M  
B. $1.8 \times 10^{-8}$ M
C. $3.6 \times 10^{-8}$ M  
D. $1.3 \times 10^{-4}$ M

3. How many moles of Pb$^{2+}$ are there in 500.0 mL of a saturated solution of PbSO$_4$?

A. $3.2 \times 10^{-16}$  
B. $9.0 \times 10^{-9}$
C. $6.7 \times 10^{-5}$  
D. $1.3 \times 10^{-4}$

Hebdon Reference: Sections III.6

Practice Exercises:

Complete the following exercises from the Hebden text:

Page 92 Exercise 41.
Page 95 Exercises 43 to 49, 51 to 54.
Page 99 Exercises 68 and 69.

C.2.3: Determining the Maximum Ion Concentrations in Solutions

Another type of equilibrium calculation that was examined in Unit 2 required us to calculate one equilibrium concentration given the $K_{eq}$ value and all other required equilibrium concentrations.

During our study of how to remove ions from solution by precipitation, we discussed the fact that the addition of Pb$^{2+}$ ions to a solution containing SO$_4^{2-}$ ions may cause the precipitation of PbSO$_4(s)$ (see pages 7 and 8 of Unit 3 Topic B).

At that time, we discussed the idea that precipitation of PbSO$_4$ will not begin until the concentration of the Pb$^{2+}$ ions and SO$_4^{2-}$ are high enough that the solution has become saturated.

In this section, we will examine how to determine the maximum concentration of a particular ion that can exist in a solution without causing a precipitate to form.
Before we do this, we must re-examine what is meant to say that a solution is *saturated*.

Let's consider a solution containing both Pb\(^{2+}\) and SO\(_{4}\)^{2-} ions at 25\(^\circ\)C. From what we have previously learned, we know that for the equilibrium:

\[
PbSO_4(s) \rightleftharpoons Pb^{2+}(aq) + SO_{4}^{2-}(aq)
\]

The Equilibrium Law expression is:

\[
K_{sp}(PbSO_4) = [Pb^{2+}][SO_{4}^{2-}] = 1.8 \times 10^{-8}
\]

We know that in a saturated solution made by dissolving solid PbSO\(_4\) into water that the concentrations of the Pb\(^{2+}\) ions and the SO\(_{4}\)^{2-} ions will be equal (because of the 1:1:1 mole ratio for the dissociation of PbSO\(_4\)). Further, we know that the two ion concentrations will be equal to the square root of the \(K_{sp}\).

However, we can form a saturated solution of PbSO\(_4\) that consists of *unequal* moles of Pb\(^{2+}\) and SO\(_{4}\)^{2-} ions. Consider the following table:

<table>
<thead>
<tr>
<th>[Pb(^{2+})]</th>
<th>[SO(_{4})^{2-}]</th>
<th>[Pb(^{2+})][SO(_{4})^{2-}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 M</td>
<td>1.8 x 10(^{-8}) M</td>
<td>1.8 x 10(^{-8})</td>
</tr>
<tr>
<td>2.68 x 10(^{-8}) M</td>
<td>6.71 x 10(^{-9}) M</td>
<td>1.8 x 10(^{-8})</td>
</tr>
<tr>
<td>1.34 x 10(^{-8}) M</td>
<td>1.34 x 10(^{-9}) M</td>
<td>1.8 x 10(^{-8})</td>
</tr>
<tr>
<td>6.71 x 10(^{-8}) M</td>
<td>2.68 x 10(^{-9}) M</td>
<td>1.8 x 10(^{-8})</td>
</tr>
<tr>
<td>1.8 x 10(^{-8}) M</td>
<td>1.0 M</td>
<td>1.8 x 10(^{-8})</td>
</tr>
</tbody>
</table>

Each of the five pairs of concentrations in the table above obeys the Equilibrium Law for PbSO\(_4\) at 25\(^\circ\)C. Thus, each combination of concentrations constitutes a solution that contains a stable amount of dissolved Pb\(^{2+}\) and SO\(_{4}\)^{2-} ions. Therefore, each combination of concentrations constitutes a saturated solution of PbSO\(_4\).

A saturated solution is one that consists of any combination of ion concentrations that obeys the Equilibrium Law for an ionic compound.

**Examples:**

1. What is the maximum concentration of Pb\(^{2+}\) ions that can exist in a solution containing 0.050 M SO\(_{4}\)^{2-} ions? (Assume T = 25\(^\circ\)C)

**Solution:**

When the solution is at its saturation point, it is in equilibrium. Essentially, this example is asking us to determine the equilibrium concentration of Pb\(^{2+}\) ions, given the \(K_{sp}\) (we have to look it up on the
appropriate table), and the equilibrium $[\text{SO}_4^{2-}]$. When the solution is at its saturation point, the equilibrium present is:

$$\text{PbSO}_4(s) \rightleftharpoons \text{Pb}^{2+}(aq) + \text{SO}_4^{2-}(aq)$$

The $K_{sp}$ expression is:

$$K_{sp} = [\text{Pb}^{2+}][\text{SO}_4^{2-}] = 1.8 \times 10^{-8}$$

Since $[\text{SO}_4^{2-}] = 0.050 \text{ M}$,

Therefore, 

$$\text{maximum } [\text{Pb}^{2+}](0.050) = 1.8 \times 10^{-8}$$

$$\text{maximum } [\text{Pb}^{2+}] = 3.6 \times 10^{-7} \text{ M}$$

2. What $[\text{Fe}^{2+}]$ will cause the precipitation of $\text{Fe(OH)}_{2(s)}$ in 0.0020 M NaOH?

**Solution:**

This problem is only slightly more difficult than the previous one.

3. Determine the maximum mass of solid $\text{Mg(NO}_3\text{)}_2$ that can dissolve in 500.0 mL of 0.025 M NaOH. Assume a negligible volume change as a result of the addition of the solid.
Provincial Exam Examples: Maximum Ion Concentration in Solutions

1. What is the maximum number of moles of Cl\(^{-}\) that can exist in 500.0 mL of 2.0 M AgNO\(_3\)?

A. 4.5 x 10\(^{-11}\)  
B. 9.0 x 10\(^{-11}\)  
C. 1.8 x 10\(^{-10}\)  
D. 1.8 x 10\(^{-9}\)

2. Which of the following ions would have the highest concentration in 0.1 M CO\(_3^{2-}\)?

A. Ba\(^{2+}\)  
B. Ca\(^{2+}\)  
C. Sr\(^{2+}\)  
D. Mg\(^{2+}\)

3. An equal number of moles of Na\(_2\)CO\(_3\) is added to four different 10.0 mL samples, each containing an equal concentration of a different ion.

<table>
<thead>
<tr>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
<th>Sample 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50 M Ba(^{2+})(_{aq})</td>
<td>0.50 M Ca(^{2+})(_{aq})</td>
<td>0.50 M Mg(^{2+})(_{aq})</td>
<td>0.50 M Sr(^{2+})(_{aq})</td>
</tr>
</tbody>
</table>

A precipitate forms in only one of the samples. Identify the cation that is present in the precipitate.

A. Ba\(^{2+}\)  
B. Mg\(^{2+}\)  
C. Ca\(^{2+}\)  
D. Sr\(^{2+}\)

4. Calculate the maximum [CO\(_3^{2-}\)] that can exist in 0.0010 M Mg(NO\(_3\))\(_2\).

5. Sufficient Na\(_2\)SO\(_4\) is added to 0.10 M Ba(NO\(_3\))\(_2\) to cause a precipitate to form.

a) Write the net ionic equation for the precipitation formation.

b) Calculate the [SO\(_4^{2-}\)] at the moment the precipitate starts to form.
6. Calculate the mass of NaI necessary to begin precipitation of Cu$^{+}$ from a 250.0 mL sample of 0.010 M CuNO$_3$.

7. Calculate the mass of solid AgNO$_3$ that can be added to 2.0 L of 0.10 M K$_2$CrO$_4$ solution in order to just start precipitation.

**C.2.4: Predicting Precipitation Reactions Using K$_{sp}$ Values**

Earlier in this unit we predicted precipitation reactions using the table of Solubility of Common Compounds in Water. Because of the definition of soluble, that table is only useful for predicting precipitation reactions if ion concentrations are greater than or equal to 0.1 M after two solutions are mixed.

When the concentrations of each of the ions after the mixing of two solutions are less than 0.1 M, we can use appropriate K$_{sp}$ values to predict precipitation reactions.

The mathematical procedure required to do this is very much like the "Trial K$_{eq}$" calculations that we did in Unit 2. However, in this case we will use the term "Trial Ion Product" or, preferably, "Trial K$_{sp}$".

To calculate a Trial K$_{sp}$ value, we first determine the concentrations of the ions that may form a precipitate immediately after two dilute solutions are mixed (we did this sort of thing in Topic 3A). These concentrations are then placed into the appropriate "Trial K$_{sp}$ expression" and the appropriate
conclusion is made based on the comparison of that value with the actual $K_{sp}$ value for the ionic compound in question.

- If the Trial $K_{sp} < \text{Actual } K_{sp}$ no precipitate forms.
- If the Trial $K_{sp} = \text{Actual } K_{sp}$ the solution is at equilibrium (i.e., at the saturation point) and no precipitate forms.
- If Trial $K_{sp} > \text{Actual } K_{sp}$ the combination of the ion concentrations immediately after the solutions are mixed exceeds those in a saturated solution and a precipitate forms.

Arriving at the correct conclusion may require that you obtain the appropriate $K_{sp}$ value from the table of Solubility Product Constants at 25ºC in the Data Booklet.

**Examples**

Show by calculation whether or not a precipitate forms when each pair of solutions is mixed.

a) 25.0 mL of $3.0 \times 10^{-3}$ M SrCl$_2$ and 75.0 mL of $8.0 \times 10^{-4}$ M Na$_2$C$_2$O$_4$ [$K_{sp}(\text{SrC}_2\text{O}_4) = 5.6 \times 10^{-8}$]

b) 20.0 mL of 0.0030 M AgNO$_3$ and 30.0 mL of 0.0060 M KIO$_3$

c) 100.0 mL of 0.0070 M CuBr$_2$ and 75.0 mL of 0.0030 M of Pb(NO$_3$)$_2$
d) 80.0 mL of 0.00060 M \( \text{Na}_2\text{CO}_3 \) and 100.0 mL of 0.00040 M \( \text{AgNO}_3 \)

**Provincial Exam Examples: The Trial \( K_{sp} \)**

1. Two salt solutions were mixed and a Trial \( K_{sp} \) was calculated to be \( 2.0 \times 10^{-9} \). The \( K_{sp} \) value is \( 1.0 \times 10^{-10} \). From this information, which of the following is a true statement?

<table>
<thead>
<tr>
<th>( K_{sp} ) Comparison</th>
<th>Outcome</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Trial ( K_{sp} &lt; K_{sp} )</td>
<td>precipitate forms</td>
</tr>
<tr>
<td>B. Trial ( K_{sp} &gt; K_{sp} )</td>
<td>precipitate forms</td>
</tr>
<tr>
<td>C. Trial ( K_{sp} &lt; K_{sp} )</td>
<td>no precipitate forms</td>
</tr>
<tr>
<td>D. Trial ( K_{sp} &gt; K_{sp} )</td>
<td>no precipitate forms</td>
</tr>
</tbody>
</table>

2. When equal volumes of 0.20 M \( \text{NaOH} \) and 0.20 M \( \text{CaS} \) are mixed together,

A. A precipitate forms and the Trial \( K_{sp} \) would be less than the \( K_{sp} \).
B. no precipitate forms and the Trial \( K_{sp} \) would be less than the \( K_{sp} \).
C. a precipitate forms and the Trial \( K_{sp} \) would be greater than the \( K_{sp} \).
D. no precipitate forms and the Trial \( K_{sp} \) would be greater than the \( K_{sp} \).

3. When a solution containing \( \text{Ag}^+ \) is mixed with a solution containing \( \text{BrO}_3^- \), the trial ion product is determined to be \( 2.5 \times 10^{-7} \). What would be observed?

A. A precipitate would form since trial ion product \( < K_{sp} \).
B. A precipitate would form since trial ion product \( > K_{sp} \).
C. A precipitate would not form since trial ion product \( < K_{sp} \).
D. A precipitate would not form since trial ion product \( > K_{sp} \).

4.a) Write the net ionic equation for the reaction between \( \text{Pb(NO}_3)_2 \) and \( \text{NaCl} \).

This example continues on the following page.
b) Determine, with calculations, whether a precipitate will form when 15.0 mL of 0.050 M Pb(NO$_3$)$_2$ is added to 35.0 mL of 0.085 M NaCl.

**Hebden Reference:** Sections III.7

**Practice Exercises:**

Complete the following exercises from the Hebden text:

Page 95 Exercises 42, 50, 55, Pages 98 to 99 Exercises 56 to 67.

C.2.5: Solubility Titrations

A titration is a quantitative analytical procedure used to determine the unknown amount (concentration, moles or mass) of a substance in a precisely measured quantity of a solution or impure solid.

The illustration to the left shows the apparatus used in a typical titration. In this case, a titration is being performed to determine the unknown [Cl$^-$] in a water sample. This is done by reacting the Cl$^-$ ions with the Ag$^+$ ions in a AgNO$_3$ solution of known concentration.

In a typical solubility titration, a precisely measured amount of the "unknown" being analyzed (called the *titrate*) is placed into an Erlenmeyer flask. If the unknown is a solid, it is usually dissolved in distilled water as an initial step.

The burette normally contains a solution of precisely known concentration, also known as the "standard solution". In every titration the substance being added to the unknown is called the *titrant*.

In simplest terms, the titrant is added to the titrate until the reaction between the two has gone to completion or near enough to completion that we can obtain a very precise result. The point at which we stop adding titrant to the titrate is called the *endpoint* of the titration.

Ideally, we end a titration when the number of moles of titrant and
titrate reacted are in agreement with the mole ratio of the reaction involved (1:1, 2:1, etc.). The point in a titration where the mole ratio is obeyed is called the stoichiometric point or the equivalence point. Ideally, the endpoint and equivalence point of a titration occur after the addition of the same amount of titrant. Unfortunately, this is rarely the case. There are a couple of reasons for this.

Firstly, many chemical reactions do not provide us with a clear indication of when equivalent moles of titrant and titrate have been combined. In the case of solubility titrations, the reaction between the titrant and titrate usually results in a precipitate that forms a cloudy suspension of solid in the mixture of the solutions in the Erlenmeyer flask. This makes it difficult for us to observe any macroscopic changes that indicate when the equivalence point has been reached.

Secondly, not all chemical reactions go to completion. For example, when a sample containing an unknown $[Cl^-]$ is titrated with a solution containing $Ag^+$ ions, the precipitation reaction is:

$$Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)}$$

However, at the point in the titration where equivalent moles of $Ag^+$ and $Cl^-$ have been mixed together, some dissolved $Cl^-$ ions will remain dissolved in solution. Because $AgCl$ is very slightly soluble, the mixture of titrant and titrate will be saturated with dissolved $AgCl$. Continuing to add $Ag^+$ beyond the equivalence point will continue to cause $AgCl_{(s)}$ to precipitate, but the $[Cl^-]$ will never be reduced to zero, nor do we want it to be.

The practice of titration usually requires the experimenter to develop some method that will indicate when the equivalence point has been reached or very nearly reached. The methods used to indicate the endpoint of a titration vary widely, but in nearly all situations, the endpoint is indicated by a colour change. This colour change is caused by the presence of a small quantity of some substance that is added before the titration begins. This substance is usually called the indicator. During the titration of a sample to determine the $[Cl^-]$ using a solution containing $Ag^+$ ions, it is common to add a small quantity of $Na_2CrO_4$ as an indicator. This substance has a distinct yellow colour.

Because $Ag_2CrO_4$ is slightly more soluble than $AgCl$ (which is a white solid), $Ag_2CrO_4$ (which is red) will begin to precipitate soon after the $[Cl^-]$ is reduced to a sufficiently low value to obtain precise results. The formation of the red solid gives a distinct indication of when to end the titration.

In any case, the volume of titrant required to reach the endpoint is used to calculate the unknown value being determined. When performing the necessary calculations, it is of utmost importance that one is aware of the mole ratio involve in the reaction. Examples of how to perform "titration calculations" follow.

Normally, titrations are repeated until two results are obtained that are equal to each other within the required precision.

**NOTE:** Hebden gives a drawn out explanation of how using $Na_2CrO_4$ as an indicator affects the precision of a titration to determine the $[Cl^-]$ in a solution (pages 99-100). You do not need to worry about this.
Examples

1. A 15.00 mL sample of well-water is analyzed to determine the unknown [Cl\textsuperscript{-}] present in it. The sample was titrated using 0.150 M AgNO\textsubscript{3}. If the endpoint of the titration is reached after the addition of 27.25 mL of titrant, determine the original [Cl\textsuperscript{-}] in the 15.00 mL sample.

2. A 28.275 g sample of impure solid BaCl\textsubscript{2} was titrated to determine its purity. The endpoint was reached after the addition of 126.40 mL of 1.875 M AgNO\textsubscript{3}. Use this information to determine the purity of the BaCl\textsubscript{2} sample, expressed as a percentage.

There is one more example on the following page.
**Provincial Exam Example: Solubility Titrations**

Consider the following information and accompanying diagram:

In a titration experiment, \( \text{AgNO}_3(\text{aq}) \) was used to determine the [Cl\(^-\)] in a water sample and the following data were recorded:

\[
\begin{align*}
\text{[AgNO}_3] &= 0.125 \text{ M} \\
\text{Volume of water sample containing [Cl}^-\text{]} &= 20.00 \text{ mL} \\
\text{Initial burette reading of AgNO}_3 &= 5.15 \text{ mL} \\
\text{Final burette reading of AgNO}_3 &= 37.15 \text{ mL}
\end{align*}
\]

The equation for the reaction is:

\[
\text{Ag}^+(\text{aq}) + \text{Cl}^-\text{(aq)} \rightarrow \text{AgCl}(s)
\]

Using the above data, determine the [Cl\(^-\)] in the water sample.

**Hebden Reference:** Sections III.8

**Practice Exercises:**

Complete the following exercises from the Hebden text:

Pages 101 and 102 Exercises 70 to 75.

It is now time to complete and submit the Unit 3 Topic C Hand-in Assignment.