SOLUBILITY EQUILIBRIUM

A. INTRODUCTION TO SOLUBILITY

1. Solutions are examples of homogeneous mixtures because they are uniform throughout. The two components of a mixture are the solute (substance in lesser concentration) and the solvent (substance in greater concentration).

2. Substances that dissolve in water can either be:

   • **ELECTROLYTE** is a substance that dissolves to give an electrically conducting solution containing ions

     e.g.  \( \text{Na}_3\text{PO}_4(s) \rightarrow 3\text{Na}^+(aq) + \text{PO}_4^{3-}(aq) \)
     \( \text{KCl}(g) \rightarrow \text{K}^+(aq) + \text{Cl}^-(aq) \)

   • **NON–ELECTROLYTE** is a substance that dissolves to give a non–conducting solution containing only neutral molecules.

     e.g.  \( \text{CH}_3\text{OH}(g) \rightarrow \text{CH}_3\text{OH}(aq) \)
     \( \text{Br}_2(l) \rightarrow \text{Br}_2(aq) \)

   **MOLECULAR SOLUTIONS** contain only neutral molecules that are **non–electrolytes**

   **IONIC SOLUTION** contains ions that are **electrolytes**

   • Ionic compounds are made up of a metal and a non–metal

     e.g.  \( \text{FeCl}_3(s) \rightarrow \text{Fe}^{3+}(aq) + 3\text{Cl}^-(aq) \)
     \( \text{Na}_2\text{SO}_4(s) \rightarrow 2\text{Na}^+(aq) + \text{SO}_4^{2-}(aq) \)

   • Molecular compounds are made up 2 non–metals (covalent)

     e.g.  \( \text{C}_2\text{H}_5\text{OH}(l) \rightarrow \text{C}_2\text{H}_5\text{OH}(aq) \)
     \( \text{ClO}_2(l) \rightarrow \text{ClO}_2(aq) \)
3. The solubility of a substance is the **maximum amount** of the substance that can dissolve in a given amount of solvent at a given temperature → **SATURATED**.

- Once a solution has been saturated with a substance, the addition of more of the substance will simply cause this extra material to accumulate in undissolved form.

**SATURATION** exists when:
- i) some undissolved material is present, and
- ii) equilibrium exists between the dissolved ions and the undissolved solid.

**SOLUBILITY** = **equilibrium concentration** of the substance in solution at a given temperature or the concentration of a saturated solution.

The solubility is often expressed as **MOLAR SOLUBILITY** where the units are \( \text{mol L}^{-1} \) (M).

4. A solution is shown to be **saturated** by writing an equation showing the **substance in equilibrium with its aqueous ions**.

\[
\text{Ag}_2\text{SO}_4 (s) \rightleftharpoons 2\text{Ag}^+(aq) + \text{SO}_4^{2-}(aq)
\]

- This equilibrium equation can be interpreted as:
  a) Solid \( \text{Ag}_2\text{SO}_4 \) dissociating into ions (**DISSOLVING REACTION**).
    \[
    \text{Ag}_2\text{SO}_4 (s) \rightarrow 2\text{Ag}^+(aq) + \text{SO}_4^{2-}(aq)
    \]
  b) \( \text{Ag}^+ \) and \( \text{SO}_4^{2-} \) ions come together and form \( \text{Ag}_2\text{SO}_4 \) (**CRYSTALLIZATION REACTION**).
    \[
    2\text{Ag}^+(aq) + \text{SO}_4^{2-}(aq) \rightarrow \text{Ag}_2\text{SO}_4 (s)
    \]

- Initially, there are few ions in solution and the **dissolving reaction predominates**. The crystallization reaction speeds up as ion concentration increases.
- Eventually, the **rate of the dissolving reaction equals the rate of the crystallization reaction and equilibrium is reached**.
B. CALCULATING SOLUBILITY AND ION CONCENTRATIONS

1. Solubility is usually expressed as molar solubility with units \( \text{mol L}^{-1} \) but it can also be expressed in terms of \( \frac{\text{g}}{\text{L}} \) or \( \frac{\text{g}}{100 \text{ mL of solution}} \). It is necessary to be able to convert between units of solubility.

**EXAMPLE 3.1 CONVERTING BETWEEN UNITS OF SOLUBILITY**

If the solubility of AgI is 3.45 g/100 mL of solution, what is the solubility in terms of g/L and mol/L?

*In terms of g/L,*

\[
\frac{3.45 \text{ g AgI}}{100 \text{ mL}} \times \frac{1000 \text{ mL}}{1.00 \text{ L}} = 34.5 \text{ g/L}
\]

*In terms of mol/L,*

\[
\frac{3.45 \text{ g AgI}}{100 \text{ mL}} \times \frac{1000 \text{ mL}}{1.00 \text{ L}} \times \frac{\text{mol}}{234.8 \text{ g}} = 0.147 \text{ mol/L}
\]

- To find solubility experimentally, it is necessary to find the mass of solute required to make a known volume of a saturated solution.
EXAMPLE 3.2 CALCULATING MOLAR SOLUBILITY FROM EXPERIMENTAL DATA

a) If 0.750 L of a saturated AgCl solution contains 2.50 g AgCl, what is the molar solubility of AgCl.

b) If the molar solubility of PbI$_2$ is $1.37 \times 10^{-3}$ M, how many grams of PbI$_2$ will dissolve in 450 mL?

\[ \text{a) First, calculate the number of moles of solute:} \]
\[ \text{moles of AgCl} = \frac{2.50 \text{ g AgCl}}{143.4 \text{ g/mol}} = 0.0174 \text{ mol} \]

\[ \text{since molar solubility is expressed in units of mol/L:} \]
\[ \text{Molar solubility} = \frac{0.0174 \text{ mol}}{0.750 \text{ L}} = 0.0232 \text{ mol/L} \]

\[ \text{b) First, calculate the number of moles of PbI}_2: \]
\[ \text{moles} = 1.37 \times 10^{-3} \frac{\text{mol}}{\text{L}} \times 0.450 \text{ L} = 6.16 \times 10^{-4} \text{ mol} \]

\[ \text{Second, calculate mass:} \]
\[ \text{mass} = 6.15 \times 10^{-4} \text{ mol} \times 461.0 \frac{\text{g}}{\text{mol}} = 0.284 \text{ g} \]

2. When an ionic compound dissolves, it **dissociates into ions.**

- It is important to be able to write balanced **DISSOCIATION EQUATIONS** as well as calculate the concentrations of each of the ions in solution.

- When writing dissociation equations, remember that **only two kinds of ions are formed** and often they will be polyatomic ions.

**DISSOCIATION EQUATION**

\[ \text{Na}_3\text{PO}_4(s) \rightarrow 3\text{Na}^+(aq) + \text{PO}_4^{3-}(aq) \]

\[ \text{Ba(NO}_3)_2(s) \rightarrow \text{Ba}^{2+}(aq) + 2\text{NO}_3^-(aq) \]
### EXAMPLE 3.3 CALCULATING ION CONCENTRATIONS

What are the concentrations of ions in 0.25 M Na$_3$PO$_4$(aq)?

*When Na$_3$PO$_4$ dissociates:*

\[
\text{Na}_3\text{PO}_4(s) \rightarrow 3\text{Na}^+(aq) + \text{PO}_4^{3-}(aq)
\]

3 moles of Na$^+$ and 1 mole of PO$_4^{3-}$ are produced from every mole of Na$_3$PO$_4$.

\[
[\text{Na}^+] = 0.25 \text{ mol/L Na}_3\text{PO}_4 \times \frac{3 \text{ Na}^+}{1 \text{ Na}_3\text{PO}_4} = 0.75 \text{ mol/L Na}^+
\]

\[
[\text{PO}_4^{3-}] = 0.25 \text{ mol/L Na}_3\text{PO}_4 \times \frac{1 \text{ PO}_4^{3-}}{1 \text{ Na}_3\text{PO}_4} = 0.25 \text{ mol/L PO}_4^{3-}
\]
EXAMPLE 3.4 CALCULATING ION CONCENTRATIONS WHEN TWO SOLUTIONS ARE ADDED

What are the concentrations of ions when 150 mL of 0.250 M Na$_3$PO$_4$(aq) is mixed with 250 mL of 0.750 M NaCl(aq)?

First, calculate the diluted concentrations of the two solutions:

\[
M_1V_1 = M_2V_2 \quad \text{so} \quad M_2 = M_1 \times \frac{V_1}{V_2}
\]

diluted concentrations are:

\[
[\text{Na}_3\text{PO}_4]_{(\text{diluted})} = 0.250 \text{ M} \times \frac{150 \text{ mL}}{400 \text{ mL}} = 0.0938 \text{ M}
\]

\[
[\text{NaCl}]_{(\text{diluted})} = 0.750 \text{ M} \times \frac{250 \text{ mL}}{400 \text{ mL}} = 0.469 \text{ M}
\]

Finally add together common ions and determine the [ions]:

\[
[\text{Na}^+] = 3(0.0938 \text{ M}) + 0.469 \text{ M} = 0.750 \text{ M}
\]

\[
[\text{PO}_4^{3-}] = 0.0938 \text{ M}
\]

\[
[\text{Cl}^-] = 0.469 \text{ M}
\]
C. PREDICTING THE SOLUBILITY OF SALTS

1. The **Solubility Table** in the Chemistry 12 Data booklet can be used to predict the solubility of various salts (ionic compounds) in water at 25 °C.

   - Strictly speaking, nothing is **INSOLUBLE** in water. Even glass will dissolve in water; however, the amount that dissolves is so small that we can ignore it and glass is said to have a **NEGLIGIBLE SOLUBILITY** in water.

   - Some substances dissolve only slightly however, the amount that does dissolve cannot be ignored. These substances are said to have **LOW SOLUBILITY**.

   > **Note:** The phrase “having a solubility less than 0.1 M” is often used to indicate low solubility.

   In addition, the statement “equal volumes of 0.2 M compound A and 0.2 M compound B are mixed” is frequently seen in questions. Since there are equal volumes of the two solutions, the concentrations will both be 0.1 M as a result of dilution. Any compound having low solubility will form a precipitate when the two solutions are mixed.

2. Consider the following section from the Solubility Table:

<table>
<thead>
<tr>
<th>NEGATIVE IONS (Anions)</th>
<th>POSITIVE IONS (Cations)</th>
<th>SOLUBILITY OF COMPOUNDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphate, PO$_4$$^{3-}$ or Carbonate, CO$_3$$^{2-}$ or Sulphite, SO$_3$$^{2-}$</td>
<td>Alkali ions, H$^+$, NH$_4$$^+$</td>
<td>Soluble</td>
</tr>
<tr>
<td></td>
<td>All others</td>
<td>LOW SOLUBILITY</td>
</tr>
</tbody>
</table>

- **Alkali ions are the ions of Group 1 and include:** Li$^+$, Na$^+$, K$^+$, Rb$^+$, Cs$^+$, Fr$^+$. According to this table, any compound that contains the anion PO$_4$$^{3-}$, CO$_3$$^{2-}$, or SO$_3$$^{2-}$ and the cations alkali ions, H$^+$, or NH$_4$$^+$ are soluble but any other cation will form compound of low solubility.

- Although the cations are not explicitly listed, they will fall under the **“all others”** category.
When two ions form a compound having “LOW SOLUBILITY”, the mixing of solutions of these two ions will form a **precipitate**.

### EXAMPLE 3.5 PREDICTING SOLUBILITY

Which of the following compounds have low solubility?

\[ \text{Na}_3\text{PO}_4, \text{MgSO}_3, \text{ZnCO}_3, (\text{NH}_4)_2\text{CO}_3 \]

*Find the negative ion (anion) on the Solubility Table:*

<table>
<thead>
<tr>
<th>NEGATIVE IONS (Anions)</th>
<th>POSITIVE IONS (Cations)</th>
<th>SOLUBILITY OF COMPOUNDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphate, PO(_4^{3-}) or Carbonate, CO(_3^{2-}) or Sulphite, SO(_3^{2-})</td>
<td>Alkali ions, H(^+), NH(_4^+)</td>
<td>Soluble</td>
</tr>
<tr>
<td></td>
<td>All others</td>
<td>LOW SOLUBILITY</td>
</tr>
</tbody>
</table>

*Next, find the positive ion (cation) and determine whether the compound is soluble or low solubility:*

\[ \text{Na}_3\text{PO}_4 \text{ and } (\text{NH}_4)_2\text{CO}_3 \text{ are both soluble} \]

\[ \text{MgSO}_3 \text{ and } \text{ZnCO}_3 \text{ fall into the all others category and are low solubility} \]
EXAMPLE 3.6 PREDICTING IF PRECIPITATES WILL FORM IN 0.1 M SOLUTIONS

Will a precipitate form when equal volumes of 0.2 M CaS and 0.2 M Na₂SO₄ are mixed?

*First, predict the products of the reaction.*
*This is a double replacement reaction so the products are:*

\[ \text{CaS} + \text{Na}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + \text{Na}_2\text{S} \]

*Next determine if either of the new product has LOW SOLUBILITY.*

\( \text{Na}_2\text{S} \) is “Soluble”

\( \text{CaSO}_4 \) has “LOW SOLUBILITY”

The precipitate that is formed is \( \text{CaSO}_4 \). (This is indicated by \( \text{CaSO}_4(s) \))

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It is useful to remember that compounds containing alkali ions (Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, Fr⁺), H⁺, NH₄⁺, or NO₃⁻ are SOLUBLE in water.

3. In some problems you will be asked to find a compound that will precipitate a particular ion. Ions do not exist on their own but rather there they are always associated with ions of the opposite charge.

- Ions are usually added compounds of soluble salts.

  Anions (–) are added as sodium salts

  Cations (+) are added as nitrate salts

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EXAMPLE 3.7 PRECIPITATING IONS

What compound could precipitate \( \text{SO}_4^{2–} \)(aq) from a solution?

*First, find a cation that forms a LOW SOLUBILITY compound with \( \text{SO}_4^{2–} \) such as \( \text{Ba}^{2+} \).
Since \( \text{Ba}^{2+} \) cannot be added on its own, it must be added a soluble salt such as \( \text{Ba(NO}_3)_2 \).
D. WRITING FORMULA, COMPLETE, AND NET IONIC EQUATIONS

1. In Chemistry 12 the reactions that produce precipitates will be DOUBLE REPLACEMENT reactions. In a double replacement reaction, the positive ion in each compound exchange.

EXAMPLE 3.8 WRITING DOUBLE REPLACEMENT REACTIONS

Write the balanced equations for the reaction of Ca(NO$_3$)$_2$ with Na$_3$PO$_4$.

First, write the formulas of the two compounds to be mixed on the reactant side.

$$\text{Ca(NO}_3\text{)}_2 + \text{Na}_3\text{PO}_4 \rightarrow \text{_______________}$$

Next, determine the charges of the ions present in the mixture (use table in data booklet if unsure).

$$\text{Ca}^{2+}, \text{NO}_3^-; \text{Na}^+, \text{PO}_4^{3-}$$

Predict the products by exchanging the two positive ions.

$$\text{Ca(NO}_3\text{)}_2 + \text{Na}_3\text{PO}_4 \rightarrow \text{Na}^+ \text{NO}_3^- + \text{Ca}^{2+} \text{PO}_4^{3-}$$

Write correct formulas for the products by canceling the ionic charges.

$$\text{Ca(NO}_3\text{)}_2 + \text{Na}_3\text{PO}_4 \rightarrow \text{Na NO}_3 + \text{Ca}_3(\text{PO}_4)_2$$

Balance the equation.

$$3 \text{ Ca(NO}_3\text{)}_2 + 2 \text{ Na}_3\text{PO}_4 \rightarrow 6 \text{ Na NO}_3 + 1 \text{ Ca}_3(\text{PO}_4)_2$$
2. Once the precipitate is determined (identified by solid \textbf{(s)} and all soluble compounds are identified as \textbf{aqueous (aq)}), you must be able to write the equation in three different ways.

a) A \textbf{FORMULA EQUATION} is a balanced chemical equation in which all the reactants are products are given by their chemical formula.

\[ 3 \text{Ca(NO}_3\text{)}_2(aq) + 2 \text{Na}_3\text{PO}_4(aq) \rightarrow 6 \text{NaNO}_3(aq) + \text{Ca}_3(\text{PO}_4)_2(s) \]

b) A \textbf{COMPLETE IONIC EQUATION} which shows all soluble compounds as ions.

\[ 3 \text{Ca}^{2+} + 6 \text{NO}_3^- + 6 \text{Na}^+ + 2 \text{PO}_4^{3-} \rightarrow 6 \text{Na}^+ + 6 \text{NO}_3^- + \text{Ca}_3(\text{PO}_4)_2(s) \]

c) A \textbf{NET IONIC EQUATION} in which all \textbf{SPECTATOR IONS are removed} from the equation. Spectator ions are ions that do not take part in the reaction and appear on both sides of the equation unchanged.

\[ 3 \text{Ca}^{2+} + 6 \text{NO}_3^- + 6 \text{Na}^+ + 2 \text{PO}_4^{3-} \rightarrow 6 \text{Na}^+ + 6 \text{NO}_3^- + \text{Ca}_3(\text{PO}_4)_2(s) \]

\[ 3 \text{Ca}^{2+} + 2 \text{PO}_4^{3-} \rightarrow \text{Ca}_3(\text{PO}_4)_2(s) \]

\textbf{Note:} If all you need is a net ionic equation, you don't need to go through all these steps. Simply determine the precipitate and write the balanced set of ions to complete the reaction.

\[ \text{_____________} \rightarrow \text{Ca}_3(\text{PO}_4)_2(s) \]

\[ 3 \text{Ca}^{2+} + 2 \text{PO}_4^{3-} \rightarrow \text{Ca}_3(\text{PO}_4)_2(s) \]
E. SEPARATING MIXTURES OF IONS BY PRECIPITATION

1. It is apparent from the Solubility Table that a cation may form a compound that is of low solubility (and hence precipitate) with one anion but soluble with another.

<table>
<thead>
<tr>
<th>NEGATIVE IONS (Anions)</th>
<th>POSITIVE IONS (Cations)</th>
<th>SOLUBILITY OF COMPOUNDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxide, OH(^{-})</td>
<td>Alkali ions, H(^{+}), NH(_4)(^{+}), Sr(^{2+})</td>
<td>Soluble</td>
</tr>
<tr>
<td></td>
<td>All others</td>
<td>LOW SOLUBILITY</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>NEGATIVE IONS (Anions)</th>
<th>POSITIVE IONS (Cations)</th>
<th>SOLUBILITY OF COMPOUNDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphate, SO(_4^{2-})</td>
<td>All others</td>
<td>Soluble</td>
</tr>
<tr>
<td></td>
<td>Ag(^{+}), Ca(^{2+}), Sr(^{2+}), Ba(^{2+}), Pb(^{2+})</td>
<td>LOW SOLUBILITY</td>
</tr>
</tbody>
</table>

- We can see that the cation Sr\(^{2+}\) will form a soluble compound with OH\(^{-}\) but it would form a low solubility compound (precipitate) with SO\(_4^{2-}\). In addition, cations such as Mg\(^{2+}\) or Fe\(^{2+}\) would precipitate OH\(^{-}\) but not SO\(_4^{2-}\) even though they are not explicitly listed in the table.

2. The ability of cations to only precipitate certain anions allows for the SELECTIVE PRECIPITATION of those ions from a solution that may contain several different anions. In addition, this principle would allow us to design a set of experiments to detect the presence of certain ions in a substance — this is the basis of QUALITATIVE ANALYSIS.
### EXAMPLE 3.9 DETECTING IONS IN SOLUTION

A solution contains either Ag⁺ and Sr²⁺ ions. Devise a method of determining which ion is present in the solution.

*The following table shows the possible reactions between the two cations and the possible anions that could be added (from Solubility Table).*

<table>
<thead>
<tr>
<th></th>
<th>Cl⁻</th>
<th>SO₄²⁻</th>
<th>S²⁻</th>
<th>OH⁻</th>
<th>PO₄³⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag⁺</td>
<td>PPT</td>
<td>PPT</td>
<td>PPT</td>
<td>PPT</td>
<td>PPT</td>
</tr>
<tr>
<td>Sr²⁺</td>
<td></td>
<td></td>
<td>PPT</td>
<td></td>
<td>PPT</td>
</tr>
</tbody>
</table>

We can see that Cl⁻, S²⁻, or OH⁻ will precipitate with the Ag⁺ but not the Sr²⁺ so the addition of any of these ions will allow us to determine which cation is present.

*Add Cl⁻, S²⁻, or OH⁻*

**PRECIPITATE** forms the solution contains Ag⁺

**NO PRECIPITATE** forms the solution contains Sr²⁺
EXAMPLE 3.10 SEPARATING IONS IN SOLUTION

A solution contains one or more of Ag\(^+\) and Ba\(^{2+}\), and Ni\(^{2+}\). Devise a method of separating each ion from the solution.

The following table shows the possible reactions among the three cations and the possible anions that could be added (from Solubility Table).

<table>
<thead>
<tr>
<th></th>
<th>Cl(^-)</th>
<th>SO(_4^{2-})</th>
<th>S(^2-)</th>
<th>OH(^-)</th>
<th>PO(_4^{3-})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag(^+)</td>
<td>PPT</td>
<td>PPT</td>
<td>PPT</td>
<td>PPT</td>
<td>PPT</td>
</tr>
<tr>
<td>Ba(^{2+})</td>
<td></td>
<td>PPT</td>
<td></td>
<td>PPT</td>
<td></td>
</tr>
<tr>
<td>Ni(^{2+})</td>
<td></td>
<td></td>
<td>PPT</td>
<td>PPT</td>
<td></td>
</tr>
</tbody>
</table>

**Step 1:** Add Cl\(^-\) to precipitate the Ag\(^+\) as AgCl(s)
Filter and remove AgCl(s)

**Step 2:** Add SO\(_4^{2-}\) to the filtrate to precipitate the Ba\(^{2+}\) as BaSO\(_4\)(s)
Filter and remove BaSO\(_4\)(s)

**Step 3:** Add S\(^2-\) to the filtrate to precipitate the Ni\(^{2+}\) as NiS(s)
Filter and remove the NiS(s)

*Note:* Once an ion has been precipitated and removed from the solution, we don’t need to worry about it precipitating in a subsequent step; however, the order that the reagents are added is important.
When substances that are only slightly soluble dissolve in water, very little is required to form a saturated solution. When the solution becomes saturated, a heterogeneous equilibrium is created between the solid and its ions. 

\[
PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)
\]

- A saturated solution is said to be a dynamic equilibrium because the rate of dissolving equals the rate of precipitation and both reactions continue to occur even though there are no macroscopic changes.
- Saturated solutions are best represented with a double arrow in their dissociation equations.

An equilibrium expression can be written for a saturated solution. This equilibrium expression is called the SOLUBILITY PRODUCT EXPRESSION. The solubility product expression for the reaction: \( PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq) \) is

\[
K_{sp} = [Pb^{2+}][Cl^-]^2 \quad K_{sp} \text{ is called the Solubility Product constant}
\]

Note: \( K_{sp} \) must be used in calculation or comparison of solubilities (refer to SOLUBILITY PRODUCT CONSTANTS AT 25°C table in data booklet); however, if you only need to predict if a compound has low solubility use the table “SOLUBILITY OF SOME COMMON COMPOUNDS IN WATER”.

The concentration for a pure solid is considered constant because it is fixed by its density. As a result, the concentration of the solid is incorporated into the equilibrium constant.

The solubility product constant or solubility product, \( K_{sp} \), is referred to as an ion product. It has no units and its expression does not have a denominator because the reactant is a solid.

- Just like \( K_{eq} \), large values for \( K_{sp} \) indicate that the products are favoured; therefore, the larger the value of \( K_{sp} \), the greater the number of ions and hence the greater the solubility of the compound.
SAMPLE 3.1 WRITING $K_{sp}$ EXPRESSIONS

Write the $K_{sp}$ expression for the following equilibria.

a) $\text{BaCrO}_4(s) \rightleftharpoons \text{Ba}^{2+} + \text{CrO}_4^{2-}$

b) $\text{Ag}_3\text{PO}_4(s) \rightleftharpoons 3\text{Ag}^+ + \text{PO}_4^{3-}$

4. Consider the following saturated solution:

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

- This equilibrium can be reached from either the reactants or the products. If this equilibrium is reached from the reactants, $\text{PbCl}_2(s)$ is simply dissolved in water and

  $[\text{Pb}^{2+}] = [\text{PbCl}_2(aq)]$

  $[\text{Cl}^-] = 2 \times [\text{PbCl}_2(aq)]$

  $[\text{Cl}^-] = 2 \times [\text{Pb}^{2+}]$

- If this equilibrium is reached from the products the above proportions are NOT necessarily true and the $[\text{Pb}^{2+}]$ and $[\text{Cl}^-]$ will depend on the solutions that are mixed together.

  e.g. What are the $[\text{Pb}^{2+}]$ and $[\text{Cl}^-]$ when 25.0 mL of 0.025 M $\text{Pb(NO}_3)_2(aq)$ is mixed with 30.0 mL of 0.010 M $\text{AlCl}_3(aq)$

  $$[\text{Pb(NO}_3)_2] = \frac{(25.0 \text{ mL})(0.025 \text{ M})}{55.0 \text{ mL}} = 0.0114 \text{ M}$$

  $$[\text{AlCl}_3] = \frac{(30.0 \text{ mL})(0.010 \text{ M})}{55.0 \text{ mL}} = 0.00545 \text{ M}$$

  $[\text{Pb}^{2+}] = [\text{Pb(NO}_3)_2] = \textbf{0.0114} \text{ M}$

  $[\text{Cl}^-] = 3 \times [\text{AlCl}_3] = \textbf{0.0164} \text{ M}$

**Note:** When solving solubility problems, it is important to know how the equilibrium was established.
G. SOLUBILITY AND SOLUBILITY PRODUCT CALCULATIONS

1. Calculations involving $K_{sp}$ are simpler than for previous equilibrium calculations because the reactant is a solid and therefore omitted from the equilibrium expression. There are really only two types of problems that need to be solved:

   a) calculating $K_{sp}$ from solubility data or

   b) calculating solubility from $K_{sp}$.

**EXAMPLE 3.11 CALCULATING $K_{sp}$ FROM SOLUBILITY DATA**

100 mL of a saturated PbI$_2$ solution was found to contain $5.23 \times 10^{-2}$ g PbI$_2$(s). Calculate $K_{sp}$.

*First need the molar solubility of PbI$_2$:*

\[
\text{Moles of PbI}_2 = \frac{5.93 \times 10^{-2} \text{ g}}{461 \text{ g/mol}} = 1.29 \times 10^{-4} \text{ mol}
\]

\[
\text{Molar solubility of PbI}_2 = \frac{1.29 \times 10^{-4} \text{ mol}}{0.100 \text{ L}} = 1.29 \times 10^{-3} \text{ mol/L}
\]

*Next calculate the concentration of the ions and substitute into the $K_{sp}$ expression:*

\[
PbI_2(s) \rightleftharpoons Pb^{2+} + 2I^-
\]

\[
[Pb^{2+}] = [PbI_2] = 1.29 \times 10^{-3} \text{ M}
\]

\[
[I^-] = 2 \times [PbI_2] = 2 (1.29 \times 10^{-3} \text{ M}) = 2.58 \times 10^{-3} \text{ M}
\]

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

\[
K_{sp} = (1.29 \times 10^{-3} \text{ M}) (2.58 \times 10^{-3} \text{ M})^2
\]

\[
K_{sp} = 8.59 \times 10^{-9}
\]
EXAMPLE 3.12 CALCULATING SOLUBILITY FROM $K_{sp}$

What is the molar solubility of PbCl$_2$ if the $K_{sp}$ of PbCl$_2$ is $1.8 \times 10^{-4}$?

First, write out the dissociation equation and the $K_{sp}$ expression:

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

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

Let $x$ be the molar solubility of PbCl$_2$

$[\text{Pb}^{2+}] = x$ and $[\text{Cl}^-] = 2x$

Substitute equilibrium values into $K_{sp}$ expression.

$$K_{sp} = (x)(2x)^2$$

$$K_{sp} = 4x^3 = 1.8 \times 10^{-4}$$

$$x = \sqrt[3]{\frac{1.8 \times 10^{-4}}{4}} = 0.0356 \text{ mol/L}$$

The molar solubility of PbCl$_2$ is 0.0356 mol/L
EXAMPLE 3.13 CALCULATING ION CONCENTRATIONS FROM $K_{sp}$

What is the $[Ag^+]$ in a saturated solution of $Ag_2CO_3$?

First, the $K_{sp}$ is needed so lookup the value of $K_{sp}$ in the Data Booklet:

$K_{sp}$ of $Ag_2CO_3 = 8.5 \times 10^{-12}$

Next, write out the dissociation equation and the $K_{sp}$ expression:

$Ag_2CO_3(s) \rightleftharpoons 2Ag^+(aq) + CO_3^{2-}(aq)$

$K_{sp} = [Ag^+]^2[CO_3^{2-}]$

Let $x$ be the molar solubility of $Ag_2CO_3$

$[Ag^+] = 2x$ and $[CO_3^{2-}] = x$

Substitute equilibrium values into $K_{sp}$ expression.

$K_{sp} = (2x)^2(x)$

$K_{sp} = 4x^3 = 8.5 \times 10^{-12}$

$x = \sqrt[3]{\frac{8.5 \times 10^{-12}}{4}} = 1.29 \times 10^{-4}$ mol/L

$[Ag^+] = 2x = 2 \times (1.29 \times 10^{-4} \text{ mol/L}) = 2.57 \times 10^{-4} \text{ mol/L}$

*This problem is the same as Example 3.12 except for the final step.*
Note: In Chemistry 12 there are only two types of salts that need to be considered: AB and AB₂.

If \( x \) is the solubility of a salt then the following relationships exist between the \( K_{sp} \) and the solubility of the salt:

\[
\begin{align*}
\text{(AB salt)} & \quad K_{sp} = x^2 \quad \text{and} \quad x = \sqrt{K_{sp}} \\
\text{(AB}_2 \text{ or A}_2\text{B salt)} & \quad K_{sp} = 4x^3 \quad \text{and} \quad x = \sqrt[3]{\frac{K_{sp}}{4}}
\end{align*}
\]

**SAMPLE 3.2 CALCULATING \( K_{sp} \) FROM SOLUBILITY**

The molar solubility of Ag\(_2\)S is \(1.3 \times 10^{-17}\) M. What is the \( K_{sp} \) for Ag\(_2\)S?

\[
K_{sp} = 4(1.3 \times 10^{-17})^3 = 8.8 \times 10^{-51}
\]

**SAMPLE 3.3 CALCULATING SOLUBILITY FROM \( K_{sp} \)**

The value of \( K_{sp} \) for AgCl is \(1.8 \times 10^{-10}\). What is the molar solubility of AgCl?

\[
x = \sqrt[3]{1.8 \times 10^{-10}} = 1.3 \times 10^{-5} \text{ M}
\]
1. Whenever two solutions containing ions are mixed, there is the possibility that a precipitate may form. **If the concentrations of the ions is 0.1 M or higher any compound having low solubility will precipitate;** however, if the concentrations of the ions is **less than 0.1 M then a calculation must be performed** to determine if a precipitate will form.

   - A **TRIAL ION PRODUCT (T.I.P.)** calculation is required to determine whether a precipitate will form when the concentration of ions is less than 0.1 M.

     For the reaction:
     \[ \text{Ag}_2\text{CO}_3(s) \rightleftharpoons 2\text{Ag}^+(aq) + \text{CO}_3^{2-}(aq) \]

     the trial ion product is:
     \[ \text{TIP} = [\text{Ag}^+]^2[\text{CO}_3^{2-}] \]

     - **TIP > K_{sp}** then **PRECIPITATE**
     - **TIP = K_{sp}** then solution is saturated, **NO PRECIPITATE**
     - **TIP < K_{sp}** then solution is not saturated, **NO PRECIPITATE**

When the ion concentrations are **less than 0.1 M**, the **TRIAL ION PRODUCT (T.I.P.)** must be calculated to determine whether or not a **PRECIPITATE** will form.
EXAMPLE 3.14 USING TRIAL ION PRODUCT (T.I.P.) TO PREDICT PRECIPITATION

If the $K_{sp}$ for PbCl$_2$ is $1.8 \times 10^{-4}$, will a precipitate form when 200.0 mL of 0.015 M NaCl is mixed with 100.0 mL of 0.060 M Pb(NO$_3$)$_2$?

First, identify the precipitate and write the net ionic equation. When NaCl(aq) is mixed with Pb(NO$_3$)$_2$(aq) the precipitate that forms is PbCl$_2$. The equation is

$$\text{PbCl}_2(s) \rightleftharpoons \text{Pb}^{2+} + 2\text{Cl}^-$$

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

$$[\text{Pb}^{2+}] = \frac{100.0 \text{ mL} \times 0.060 \text{M}}{300.0 \text{ mL}} = 0.020 \text{M}$$

$$[\text{Cl}^-] = \frac{200.0 \text{ mL} \times 0.015 \text{M}}{300.0 \text{ mL}} = 0.010 \text{M}$$

Since these values are not at equilibrium, we will call this an ion product.

$$T.I.P. = [\text{Pb}^{2+}][\text{Cl}^-]^2$$

$$T.I.P. = (0.020)(0.010)^2 = 2.0 \times 10^{-6}$$

$$2.0 \times 10^{-6} < 1.8 \times 10^{-4} \rightarrow \text{no precipitate will form}$$
I. HETEROGENEOUS EQUILIBRIA AND LE CHATELIER’S PRINCIPLE

1. Heterogeneous equilibrium like all other equilibria will follow Le Chatelier’s Principle.

   **LE CHATELIER’S PRINCIPLE**

   When a stress is applied to a system at equilibrium, the system readjusts to relieve or offset the stress and the system reaches a new state of equilibrium.

Consider the following equilibrium:

\[ \text{PbCl}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2\text{Cl}^-(aq) \]

The forward reaction is the dissolving reaction:

\[ \text{PbCl}_2(s) \rightarrow \text{Pb}^{2+}(aq) + 2\text{Cl}^-(aq) \]

- If we can cause the equilibrium to **SHIFT TO THE RIGHT** then the rate of dissolving is increased more than the rate of crystallization and more solid PbCl₂ will dissolve and its **SOLUBILITY INCREASES**.

The reverse reaction is the crystallization reaction:

\[ \text{PbCl}_2(s) \leftarrow \text{Pb}^{2+}(aq) + 2\text{Cl}^-(aq) \]

- If we cause the equilibrium to **SHIFT TO THE LEFT** then the rate of crystallization is increased more than the rate of dissolving. More Pb²⁺ ions and Cl⁻ ions will combine to form solid PbCl₂ and its **SOLUBILITY DECREASES**.

2. Consider the following equilibrium:

\[ \text{PbCl}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2\text{Cl}^-(aq) \]

- The solubility of the PbCl₂(s) can be **DECREASED by increasing either [Pb²⁺] or [Cl⁻]**.
- The [Pb²⁺] can be increased by adding the soluble salt Pb(NO₃)₂.

\[ \text{PbCl}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2\text{Cl}^-(aq) \]
• The \([\text{Cl}^-]\) can be increased by adding the soluble salt \(\text{NaCl}\).

\[
PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\text{Cl}^-(aq)
\]

**COMMON ION EFFECT** = Decreasing the solubility of a salt by adding another salt with similar ions.

3. Consider the following equilibrium:

\[
PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\text{Cl}^-(aq)
\]

• The solubility of the \(\text{PbCl}_2(s)\) can be **INCREASED** by decreasing either \([\text{Pb}^{2+}]\) or \([\text{Cl}^-]\).

• The \([\text{Pb}^{2+}]\) can be decreased by adding some ion which precipitates the \(\text{Pb}^{2+}\). From the Solubility Table, any of the following ions: \(\text{Br}^-, \text{I}^-, \text{SO}_4^{2-}, \text{S}^{2-}, \text{OH}^-, \text{PO}_4^{3-}, \text{CO}_3^{2-}, \text{SO}_3^{2-}\), will precipitate \(\text{Pb}^{2+}\) (we don’t consider adding \(\text{Cl}^-\) because it is already involved in the equilibrium).

• Add a soluble salt of \(\text{Br}^-\) such as \(\text{NaBr}\):

\[
PbCl_2(s) \rightleftharpoons \downarrow \text{Pb}^{2+}(aq) + 2\text{Cl}^-(aq) + \downarrow \text{Br}-(aq)
\]

**Note:** Precipitate must have a lower solubility than the \(\text{PbCl}_2\). From the **Solubility Product Constants Table**, \(\text{PbCl}_2\) has a \(K_{sp} = 1.2 \times 10^{-5}\), so the \(K_{sp}\) of the precipitate must be lower than this value. \(\text{PbBr}_2\) has a \(K_{sp} = 6.6 \times 10^{-6}\), so we can add a soluble salt of \(\text{Br}^-\) to increase the solubility of \(\text{PbCl}_2\).

• Similarly, \(\text{Ag}^+\) can be added as \(\text{AgNO}_3\) to decrease \([\text{Cl}^-]\).

\[
PbCl_2(s) \rightleftharpoons \downarrow \text{Pb}^{2+}(aq) + \downarrow 2\text{Cl}^-(aq) + \downarrow \text{Ag}^+(aq) + \downarrow \text{AgCl}(s)
\]