# 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. $Na_3PO_4(s) \rightarrow 3Na^+(aq) + PO_4^{3-}(aq)$
              $KCl(g) \rightarrow K^+(aq) + Cl^-(aq)$
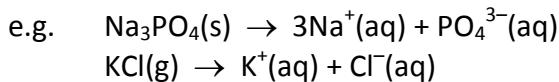
   - **NON–ELECTROLYTE** is a substance that dissolves to give a **non–conducting solution containing only neutral molecules.**

     e.g. $CH_3OH(g) \rightarrow CH_3OH(aq)$
              $Br_2(l) \rightarrow Br_2(aq)$
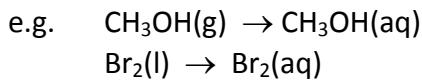
   > **MOLECULAR SOLUTIONS** contain only neutral molecules that are **non–electrolytes**
   >
   > **IONIC SOLUTION** contains ions that are **electrolytes**

   - Ionic compounds are made up of a **metal and a non–metal**

     e.g. $FeCl_3(s) \rightarrow Fe^{3+}(aq) + 3Cl^-(aq)$
              $Na_2SO_4(s) \rightarrow 2Na^+(aq) + SO_4^{2-}(aq)$
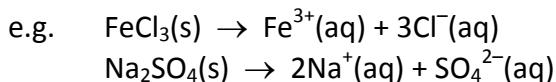
   - Molecular compounds are made up **2 non–metals (covalent)**

     e.g. $C_2H_5OH(l) \rightarrow C_2H_5OH(aq)$
              $ClO_2(l) \rightarrow ClO_2(aq)$
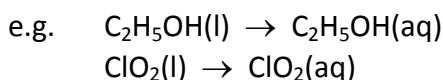
3. The solubility of a substance is the **maximum amount** of the substance that can dissolve in a given amount of solvent at a given temperature → **SATURATED**.

    - 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 $\frac{mol}{L}$ (M).

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

    $$Ag_2SO_4(s) \rightleftharpoons 2Ag^+(aq) + SO_4^{2-}(aq)$$

    - This equilibrium equation can be interpreted as:

    a) Solid Ag_2SO_4 dissociating into ions **(DISSOLVING REACTION)**.
    $$Ag_2SO_4(s) \rightarrow 2Ag^+(aq) + SO_4^{2-}(aq)$$

    b) Ag^+ and SO_4^{2-} ions come together and form Ag_2SO_4 **(CRYSTALLIZATION REACTION)**.
    $$2Ag^+(aq) + SO_4^{2-}(aq) \rightarrow Ag_2SO_4(s)$$
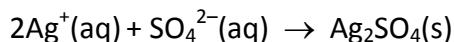
    - Initially, there are few ions in solution and the **dissolving reaction predominates.** The crystallization reaction speeds up as ion concentration increases.
    - Eventually, the **rate of the dissolving reaction equals the rate of the crystallization reaction and equilibrium is reached.**
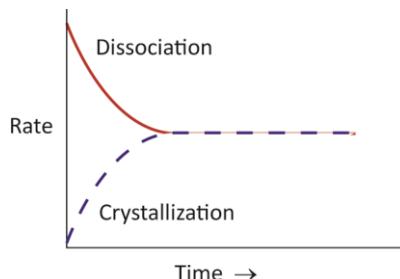
B.	**CALCULATING SOLUBILITY AND ION CONCENTRATIONS**

1. Solubility is usually expressed as **molar solubility** with units $\frac{mol}{L}$ but it can also be expressed in terms of $\frac{g}{L}$ or $\frac{g}{100 \text{ mL of solution}}$. 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,

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

In terms of mol/L,

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

- 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 1.37×10^{-3} M, how many grams of PbI_2 will dissolve in 450 mL?

> *a)   First, calculate the number of moles of solute:*
>
> $$moles\ of\ AgCl = \frac{2.50\ g\ AgCl}{143.4\ g/mol} = 0.0174\ mol$$
>
> *since molar solubility is expressed in units of mol/L:*
>
> $$Molar\ solubility = \frac{0.0174\ mol}{0.750\ L} = \textbf{0.0232 mol/L}$$
>
> *b)   First, calculate the number of moles of PbI_2:*
>
> $$moles = 1.37 \times 10^{-3}\ \frac{mol}{L} \times 0.450\ L = 6.16 \times 10^{-4}\ mol$$
>
> *Second, calculate mass:*
>
> $$mass = 6.15 \times 10^{-4}\ mol \times 461.0\ \frac{g}{mol} = \textbf{0.284 g}$$

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

$Na_3PO_4(s) \rightarrow 3Na^+(aq) + PO_4^{3-}(aq)$

$Ba(NO_3)_2(s) \rightarrow Ba^{2+}(aq) + 2NO_3^-(aq)$
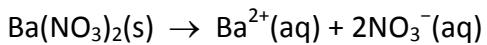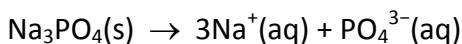
EXAMPLE 3.3 CALCULATING ION CONCENTRATIONS

What are the concentrations of ions in 0.25 M $Na_3PO_4(aq)$?

When Na_3PO_4 dissociates:

$$Na_3PO_4(s) \rightarrow 3Na^+(aq) + PO_4^{3-}(aq)$$

3 moles of Na^+ and 1 mole of PO_4^{3-} are produced from every mole of Na_3PO_4.

$$[Na^+] = 0.25 \text{ mol/L } Na_3PO_4 \times \frac{3 \text{ } Na^+}{1 \text{ } Na_3PO_4} = 0.75 \text{ mol/L } Na^+$$

$$[PO_4^{3-}] = 0.25 \text{ mol/L } Na_3PO_4 \times \frac{1 \text{ } PO_4^{3-}}{1 \text{ } Na_3PO_4} = 0.25 \text{ mol/L } PO_4^{3-}$$

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_3PO_4(aq) is mixed with 250 mL of 0.750 M NaCl(aq)?

First, calculate the diluted concentrations of the two solutions:

$$M_1V_1 = M_2V_2 \ \ so \ \ M_2 = M_1 \times \frac{V_1}{V_2}$$

diluted concentrations are:

$$[Na_3PO_4]_{(diluted)} = 0.250 \ M \times \frac{150 \ mL}{400 \ mL} = 0.0938 \ M$$

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

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

$$[Na^+] = 3(0.0938 \ M) + 0.469 \ M = 0.750 \ M$$

$$[PO_4{}^{3-}] = 0.0938 \ M$$

$$[Cl^-] = 0.469 \ M$$

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**.

A substance has **LOW SOLUBILITY** if it requires **less than 0.1 M to make a saturated solution.**

    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:

NEGATIVE IONS (Anions)	POSITIVE IONS (Cations)	SOLUBILITY OF COMPOUNDS
Phosphate, PO_4^{3-} or Carbonate, CO_3^{2-} or Sulphite, SO_3^{2-}	Alkali ions, H^+, NH_4^+	Soluble
	All others	LOW SOLUBILITY

    *   **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?

$$Na_3PO_4, MgSO_3, ZnCO_3, (NH_4)_2CO_3$$
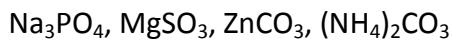
Find the negative ion (anion) on the Solubility Table:

NEGATIVE IONS (Anions)	POSITIVE IONS (Cations)	SOLUBILITY OF COMPOUNDS
Phosphate, PO_4^{3-} or Carbonate, CO_3^{2-} or Sulphite, SO_3^{2-}	Alkali ions, H^+, NH_4^+	Soluble
	All others	LOW SOLUBILITY

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

*Na_3PO_4 and $(NH_4)_2CO_3$ are both **soluble***

*$MgSO_3$ and $ZnCO_3$ 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 Na_2SO_4 are mixed?

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

*$CaS + Na_2SO_4 \rightarrow$ **$CaSO_4 + Na_2S$***

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

*Na_2S is **"Soluble"***

*$CaSO_4$ has **"LOW SOLUBILITY"***

The precipitate that is formed is $CaSO_4$. (This is indicated by $CaSO_4(s)$)

It is useful to remember that compounds containing **alkali ions (Li^+, Na^+, K^+, Rb^+, Cs^+, Fr^+), H^+, NH_4^+, or NO_3^- 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.

• Ion are usually added compounds of **soluble salts.**

Anions (–) are added as **sodium** salts

Cations (+) are added as **nitrate** salts

EXAMPLE 3.7 PRECIPITATING IONS

What compound could precipitate SO_4^{2-}(aq) from a solution?

*First, find a cation that forms a **LOW SOLUBILITY** compound with SO_4^{2-} such as Ba^{2+}.*
Since Ba^{2+} cannot be added on its own, it must be added a soluble salt such as $Ba(NO_3)_2$.

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_3PO_4.

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

$$Ca(NO_3)_2 + Na_3PO_4 \rightarrow _____$$

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

$$Ca^{2+}, NO_3^-, Na^+, PO_4^{3-}$$

Predict the products by exchanging the two positive ions.

$$Ca(NO_3)_2 + Na_3PO_4 \rightarrow Na^+ NO_3^- + Ca^{2+} PO_4^{3-}$$

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

$$Ca(NO_3)_2 + Na_3PO_4 \rightarrow Na\,NO_3 + Ca_3(PO_4)_2$$

Balance the equation.

$$3\,Ca(NO_3)_2 + 2\,Na_3PO_4 \rightarrow 6\,Na\,NO_3 + 1\,Ca_3(PO_4)_2$$

2.   Once the precipitate is determined (identified by **solid (s)** and all soluble compounds are identified as **aqueous (aq)**), you must be able to write the equation in three different ways.

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

$$3\ Ca(NO_3)_2(aq) + 2\ Na_3PO_4(aq) \rightarrow 6\ NaNO_3(aq) + Ca_3(PO_4)_2(s)$$
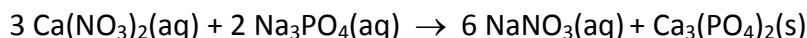
b) A **COMPLETE IONIC EQUATION** which shows all soluble compounds as ions.

$$3\ Ca^{2+} + 6\ NO_3^- + 6\ Na^+ + 2\ PO_4^{3-} \rightarrow 6\ Na^+ + 6\ NO_3^- + \textbf{Ca}_3\textbf{(PO}_4\textbf{)}_2\textbf{(s)}$$
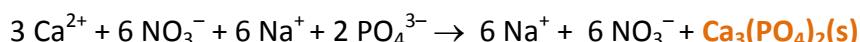
c) A **NET IONIC EQUATION** in which all **SPECTATOR IONS are removed** from the equation. Spectator ions are ions that do not take part in the reaction and appear on both sides of the equation unchanged.

$$3\ Ca^{2+} + \textbf{6 NO}_3^- + \textbf{6 Na}^+ + 2\ PO_4^{3-} \rightarrow \textbf{6 Na}^+ + \textbf{6 NO}_3^- + Ca_3(PO_4)_2(s)$$

$$\textbf{3 Ca}^{2+} + \textbf{2 PO}_4^{3-} \rightarrow \textbf{Ca}_3\textbf{(PO}_4\textbf{)}_2\textbf{(s)}$$
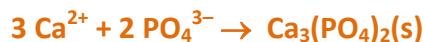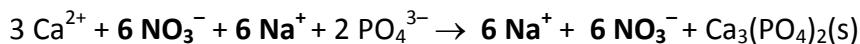
Note: If all you need is a net ionic equation, you don't need to go through all these steps. Simply determine the precipitate and write the balanced set of ions to complete the reaction.

$$\underline{\hspace{3cm}} \rightarrow Ca_3(PO_4)_2(s)$$

$$3\ Ca^{2+} + 2\ PO_4^{3-} \rightarrow Ca_3(PO_4)_2(s)$$
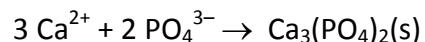
E.	SEPARATING MIXTURES OF IONS BY PRECIPITATION

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.

NEGATIVE IONS (Anions)	POSITIVE IONS (Cations)	SOLUBILITY OF COMPOUNDS
Hydroxide, OH^-	Alkali ions, H^+, NH_4^+, Sr^{2+}	Soluble
	All others	LOW SOLUBILITY

NEGATIVE IONS (Anions)	POSITIVE IONS (Cations)	SOLUBILITY OF COMPOUNDS
Sulphate, SO_4^{2-}	All others	Soluble
	Ag^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}	LOW SOLUBILITY

- 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 Sr^{2+} 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).

	Cl-	SO_4^{2-}	S^{2-}	OH^-	PO_4^{3-}
Ag^+	PPT	PPT	PPT	PPT	PPT
Sr^{2+}		PPT			PPT

We can see that Cl^-, S^{2-}, or OH^- will precipitate with the Ag^+ but not the Sr^{2+}
so the addition of any of these ions will allow us to determine which cation is present.

Add Cl^-, S^{2-}, or OH^-

PRECIPITATE *forms the solution contains Ag^+*

NO PRECIPITATE *forms the solution contains Sr^{2+}*

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).

	Cl-	SO_4^{2-}	S^{2-}	OH^-	PO_4^{3-}
Ag^+	PPT	PPT	PPT	PPT	PPT
Ba^{2+}		PPT		PPT	PPT
Ni^{2+}			PPT	PPT	PPT

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.*

F. THE SOLUBILITY PRODUCT

1. 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.**

$$PbCl_2(s) \rightleftarrows Pb^{2+}(aq) + 2Cl^-(aq)$$
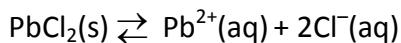
   - A saturated solution is said to be a **dynamic equilibrium** because the rate of dissolving equals the rate of precipitation and both reactions continue to occur even though there are no macroscopic changes.
   - Saturated solutions are best represented with a **double arrow in their dissociation equations.**

2. 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: $PbCl_2(s) \rightleftarrows Pb^{2+}(aq) + 2Cl^-(aq)$ is

$K_{sp} = [Pb^{2+}][Cl^-]^2$ **K_{sp} 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.

3. 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) $BaCrO_4(s) \rightleftharpoons Ba^{2+} + CrO_4^{2-}$

b) $Ag_3PO_4(s) \rightleftharpoons 3Ag^+ + PO_4^{3-}$

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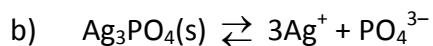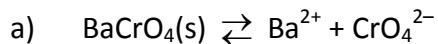
4.   Consider the following saturated solution:

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$
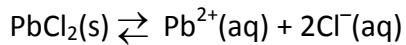
- This equilibrium can be **reached from either the reactants or the products.** If this equilibrium is reached from the **reactants**, $PbCl_2(s)$ is simply dissolved in water and

$$[Pb^{2+}] = [PbCl_2(aq)]$$

$$[Cl^-] = 2 \times [PbCl_2(aq)]$$

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

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

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

$$[Pb(NO_3)_2] = \frac{(25.0 \text{ mL})(0.025 \text{ M})}{55.0 \text{ mL}} = 0.0114 \text{ M}$$

$$[AlCl_3] = \frac{(30.0 \text{ mL})(0.010 \text{ M})}{55.0 \text{ mL}} = 0.00545 \text{ M}$$

$$[Pb^{2+}] = [Pb(NO_3)_2] = \textbf{0.0114 M}$$

$$[Cl^-] = 3 \times [AlCl_3] = \textbf{0.0164 M}$$

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 5.23×10^{-2} g $PbI_2(s)$. Calculate K_{sp}.

First need the molar solubility of PbI_2:

$$Moles\ of\ PbI_2 = \frac{5.93\ x\ 10^{-2}\ g}{461\ g/mol} = 1.29 \times 10^{-4}\ mol$$

$$Molar\ solubility\ of\ PbI_2 = \frac{1.29\ x\ 10^{-4}\ mol}{0.100\ L} = 1.29 \times 10^{-3}\ mol/L$$

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

$$PbI_2(s) \rightleftarrows Pb^{2+} + 2I^-$$

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

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

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

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

$$K_{sp} = \boldsymbol{8.59 \times 10^{-9}}$$

EXAMPLE 3.12 CALCULATING SOLUBILITY FROM K_{sp}

What is the molar solubility of $PbCl_2$ if the K_{sp} of $PbCl_2$ is 1.8×10^{-4}?

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

$$PbCl_2(s) \rightleftarrows Pb^{2+}(aq) + 2Cl^-(aq)$$
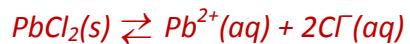
$$K_{sp} = [Pb^{2+}][Cl^-]^2$$

*Let x **be the molar solubility of PbCl₂***

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

Substitute equilibrium values into K_{sp} expression.

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

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

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

The molar solubility of PbCl₂ 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:
$Ag_2CO_3\,(s) \rightleftarrows 2Ag^+(aq) + CO_3{}^{2-}(aq)$

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

*Let x **be the molar solubility of Ag$_2$CO$_3$***
$[Ag^+] = 2x$ and $[CO_3{}^{2-}] = x$

Substitute equilibrium values into K_{sp} expression.

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

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

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

*$[Ag^+] = 2x = 2\,(1.29 \times 10^{-4}$ mol/L$) = $ **2.57 × 10^{-4} 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 AB_2.

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

$$\text{(AB salt)} \quad K_{sp} = x^2 \quad \text{and} \quad x = \sqrt{K_{sp}}$$

$$\text{(AB}_2\text{ or A}_2\text{B salt)} \quad K_{sp} = 4x^3 \quad \text{and} \quad x = \sqrt[3]{\frac{K_{sp}}{4}}$$

SAMPLE 3.2 CALCULATING K_{SP} FROM SOLUBILITY

The molar solubility of Ag_2S is 1.3×10^{-17} M. What is the K_{sp} for Ag_2S?

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

**SAMPLE 3.3 CALCULATING SOLUBILITY FROM K_{SP}**

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

$$x = \sqrt{1.8 \times 10^{-10}} = 1.3 \times 10^{-5} \, M$$

H.   PREDICTING WHETHER A PRECIPITATE WILL FORM

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:

    $$Ag_2CO_3(s) \;\rightleftarrows\; 2Ag^+(aq) + CO_3^{2-}(aq)$$
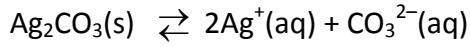
    the trial ion product is:

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

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 1.8×10^{-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

$$PbCl_2(s) \rightleftarrows Pb^{2+} + 2Cl^-$$
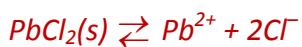
$$K_{sp} = [Pb^{2+}][Cl^-]^2$$

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

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

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

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

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

$$2.0 \times 10^{-6} < 1.8 \times 10^{-4} \rightarrow \text{no precipitate will form}$$

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:

$$PbCl_2(s) \rightleftarrows Pb^{2+}(aq) + 2Cl^-(aq)$$
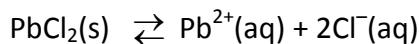
The forward reaction is the dissolving reaction:

$$PbCl_2(s) \rightarrow Pb^{2+}(aq) + 2Cl^-(aq)$$
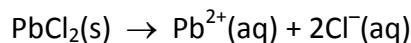
- If we can cause the equilibrium to **SHIFT TO THE RIGHT** then the rate of dissolving is increased more than the rate of crystallization and more solid $PbCl_2$ will dissolve and its **SOLUBILITY INCREASES.**

The reverse reaction is the crystallization reaction:

$$PbCl_2(s) \leftarrow Pb^{2+}(aq) + 2Cl^-(aq)$$
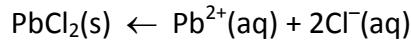
- If we cause the equilibrium to **SHIFT TO THE LEFT** then the rate of crystallization is increased more than the rate of dissolving. More Pb^{2+} ions and Cl^- ions will combine to form solid $PbCl_2$ and its **SOLUBILITY DECREASES.**

2. Consider the following equilibrium:

$$PbCl_2(s) \rightleftarrows Pb^{2+}(aq) + 2Cl^-(aq)$$
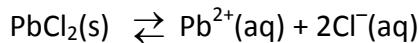
- The solubility of the $PbCl_2(s)$ can be **DECREASED by increasing either [Pb^{2+}] or [Cl$^-$].**
- The [Pb^{2+}] can be increased by adding the soluble salt **Pb(NO$_3$)$_2$.**

$$PbCl_2(s) \; \rightleftarrows \; \uparrow\mathbf{Pb^{2+}}(aq) + 2Cl^-(aq)$$

- The [Cl⁻] can be increased by adding the soluble salt Na**Cl**.

$$PbCl_2(s) \;\rightleftharpoons\; Pb^{2+}(aq) + {\uparrow}\mathbf{2Cl^-}(aq)$$
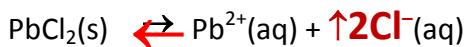
COMMON ION EFFECT = Decreasing the solubility of a salt by adding another salt with similar ions.

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3. Consider the following equilibrium:

$$PbCl_2(s) \;\rightleftharpoons\; Pb^{2+}(aq) + 2Cl^-(aq)$$
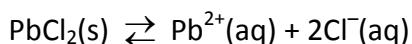
- The solubility of the $PbCl_2(s)$ can be **INCREASED by decreasing either $[Pb^{2+}]$ or $[Cl^-]$.**

- The **$[Pb^{2+}]$ can be decreased by adding some ion which precipitates the Pb^{2+}.** From the Solubility Table, any of the following ions: Br^-, I^-, SO_4^{2-}, S^{2-}, OH^-, PO_4^{3-}, CO_3^{2-}, SO_3^{2-}, will precipitate Pb^{2+} (we don't consider adding Cl^- because it is already involved in the equilibrium).

- Add a soluble salt of Br^- such as NaBr:

$$PbCl_{2(s)} \;\rightleftharpoons\; {\downarrow}Pb^{2+}{}_{(aq)} + 2Cl^-{}_{(aq)}$$
$$+$$
$$Br\text{-}$$
$$\downarrow$$
$$PbBr_{2(s)}$$
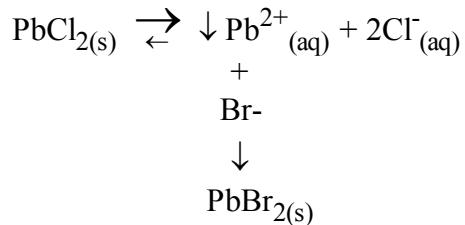
Note: Precipitate must have a lower solubility than the $PbCl_2$. From the **Solubility Product Constants Table**, $PbCl_2$ has a $K_{sp} = 1.2 \times 10^{-5}$, so the K_{sp} of the precipitate must be lower than this value. $PbBr_2$ has a $K_{sp} = 6.6 \times 10^{-6}$, so we can add a soluble salt of Br^- to increase the solubility of $PbCl_2$.

- Similarily, **Ag^+ can be added as $AgNO_3$ to decrease $[Cl^-]$.**

$$PbCl_{2(s)} \;\rightleftharpoons\; Pb^{2+}{}_{(aq)} + {\downarrow}2Cl^-{}_{(aq)}$$
$$+$$
$$Ag^+$$
$$\downarrow$$
$$AgCl_{(s)}$$