# Unit 3 - Solubility Equilibrium

- Why do some chemicals dissolve and others do not? The short answer is waters attraction is greater than the internal attractive forces of the material being dissolved. (polarity of water, etc.)
- An \_\_\_\_\_\_ is a substance that dissolves to give an electrically conducting solution containing ions.  $\underline{Ex.} - HCl_{(g)} \rightarrow H^{+}_{(aq)} + Cl^{-}_{(aq)}$
- A non-electrolyte \_\_\_\_\_
  - $\underline{\mathsf{Ex}}_{\cdot} \mathsf{C}_2\mathsf{H}_{2\,(g)} \rightarrow \mathsf{C}_2\mathsf{H}_{2\,(aq)}$
- Ionic molecules are typically made of a metal and a non-metal and they dissolve by <u>dissociation</u>. Recall that dissociation is the act of breaking into ions when the substance dissolves. <u>Ex.</u> -
- Molecular compounds (also called covalent) are typically a non-metal and a non-metal, especially organic compounds form molecular solutions. <u>Ex.</u>  $CH_3OH_{(1)} \rightarrow CH_3OH_{(aq)}$  \*\*organic as it starts with carbon\*\*
- Some covalent molecules, with ionic characteristics, dissolve by \_\_\_\_\_
- The <u>solubility</u> of a substance is the maximum amount of the substance which can dissolve in a given amount of solvent at a given temperature.
- A solution that has dissolved all the solute such that addition of anymore solute caused it to accumulate on the bottom is said to be \_\_\_\_\_\_.
- \*\*\* In chemistry 12 we should now understand that a substance is said to form a saturated solution if the dissolved substance is in equilibrium with some of the undissolved substance. \*\*\*
- So . . . to have a saturated solution the following two conditions must be met.



- You can show that a solution is saturated by writing an equation showing the substances in equilibrium.

 $AgBrO_{3(s)} \rightleftharpoons Ag^{+}(aq) + BrO_{3}^{-}(aq)$ 

- Such an equilibrium can also be interpreted as:

 $AgBrO_{3(s)} \rightarrow Ag^{+}_{(aq)} + BrO_{3}^{-}_{(aq)} =$ 

- Or also as:  $\rightarrow$   $Ag^{+}_{(aq)} + BrO_{3}^{-}_{(aq)} \rightarrow AgBrO_{3}_{(s)} =$ 

### Calculating Solubility and Ion Concentrations

### Chemistry 11 - Review

- Solubilities of ions are temperature dependent. As such, assume all solutions are at a temperature of 25°C unless otherwise stated in the question.
- <u>Ex. 1</u> It is experimentally discovered that 1.0 L of saturated AgNO<sub>3 (aq)</sub> contains 1.96 g of AgNO<sub>3</sub>. What is the molar solubility (Molarity) of AgNO<sub>3</sub>?
   <u>Answer</u> -
- <u>Ex. 2</u> The molarity of PbI<sub>2</sub> is  $1.37 \times 10^{-3}M$ . What is the solubility in grams per litre? <u>Answer</u> -
- <u>Ex. 3</u> It is experimentally discovered that 250 mL of saturated CaCl<sub>2</sub> contains 18.6 g of CaCl<sub>2</sub> at 20°C.
   What is the molarity of AgNO<sub>3</sub>?
   <u>Answer</u> -
- <u>Ex. 4</u> What is the concentration of all ions present in a saturated solution of  $Ag_2CO_3$  having a concentration of  $1.2 \times 10^{-4} M$ ? <u>Answer</u> - First write the dissociation equation

So . . . .

- <u>Ex. 5</u> - If 5.0 mL of  $0.020 \text{ }M \text{ }Cl^-$  is added to 15.0 mL of  $0.012 \text{ }M \text{ }Br^-$  what is the molarity of the Cl<sup>-</sup> and Br<sup>-</sup> ions in the mixture?

<u>Answer</u> - \*\*\*Remember how to do dilutions!!!!\*\*\*  $C_{conc} \times V_{conc} = C_{dil} \times V_{dil}$ [ $Cl^{-}$ ]<sub>dil</sub> =

 $[Br^{-}]_{dil} =$ 

- A complete ionic equation is a chemical equation with all the soluble ionic species broken into their respective ions.  $Ex. - 2 Ag^+ + 2 NO_3^- + 2 Na^+ + CO_3^{-2} \rightarrow Ag_2CO_{3(s)} + 2 Na^+ + 2 NO_3^{-2}$
- A net ionic equation is a chemical equation showing only the species which are actively involved in the reaction. This implies that any "spectator ions" should not be written.

Summary - three equation types

- 1.) 2  $AgNO_{3(aq)}$  +  $Na_2CO_{3(aq)} \rightarrow Ag_2CO_{3(s)}$  + 2  $NaNO_{3(aq)}$
- 2.) 2  $Ag^{+}$  + 2  $NO_{3}^{-}$  + 2  $Na^{+}$  +  $CO_{3}^{-2} \rightarrow Ag_{2}CO_{3(s)}$  + 2  $Na^{+}$  + 2  $NO_{3}^{-1}$
- 3.) 2 Ag<sup>+</sup> (aq) +  $CO_3^{-2}$  (aq)  $\rightarrow$  Ag<sub>2</sub>CO<sub>3 (s)</sub>

#### The Solubility Product

- Like we learned in the second unit this year, chemical equations have an equilibrium expression or  $K_{eq}$ . When the equilibrium expression applies to the <u>dissociation of a salt reaction</u> we call it the \_\_\_\_\_

\_\_\_\_\_ and the short form expression is K<sub>sp</sub>.

 $\underbrace{\text{Ex.}}_{\text{Now}} \rightarrow CaF_{2(s)} \rightleftharpoons Ca^{+2}_{(aq)} + 2F_{(aq)} \qquad K_{eq} = [Ca^{+2}] + [F^{-}]^{2}$   $Now \rightarrow CaF_{2(s)} \leftrightharpoons Ca^{+2}_{(aq)} + 2F_{(aq)} \qquad K_{sp} = [Ca^{+2}] + [F^{-}]^{2} = 1.46 \times 10^{-10} \quad (--\text{ dissolving a salt})$ 

- How soluble a salt is in water can be expressed as a number, hello  $K_{sp}$ !

- So, the larger a K<sub>sp</sub> value is the greater that salt will dissolve in water. A <u>chart of K<sub>sp</sub> values</u> is contained in your data booklet.

#### \*\*\*\*\*Reminder\*\*\*\*\*

- Solubility is the amount of substance required to make a saturated solution.
- Solubility Product is the K<sub>sp</sub> value obtained when the concentrations of the ions in a saturated solution are multiplied together.
- A generic equation where the initial chemicals solubility constant is  $4.3 \times 10^{-4}$ .

- Let's look at some examples now of how the solubility product can be solved for.

 $\underline{Ex.\,1}$  -  $K_{sp}$   $\rightarrow$  Solubility for AB compounds

 $K_{sp}$  for  $AgCl = 1.8 \times 10^{-10}$  What is the solubility of the  $Ag^{+}$  and  $Cl^{-2}$ 

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

<u>Ex. 2</u> -  $K_{sp} \rightarrow$  Solubility for AB<sub>2</sub> (ex. - Mg(OH)<sub>2</sub>)

- If a solution of Mg(OH)<sub>2</sub> at a certain temperature =  $0.24 \frac{g}{L}$  what is K<sub>sp</sub>?

<u>Ex. 3</u> -  $K_{sp} \rightarrow$  Solubility for  $A_2B$  compounds (ex. -  $Ag_2CrO_4$ )

- A solution of Ag<sub>2</sub>CrO<sub>4</sub>.  $K_{sp} = 1.1 \times 10^{-12}$ 

- There is only a couple of types of problems to do in this section and none of them involve ICE boxes.

1.) Given solubility  $\rightarrow$  solve for  $K_{sp}$ 

<u>Ex.</u> - The solubility of AgBr is  $8.8 \times 10^{-7} \frac{mol}{L}$ . Calculate the K<sub>sp</sub>.

<u>Answer</u> - Write equilibrium equation

Ratio -

[] -Write equilibrium expression

<u>Ex.</u> - The solubility of Fe(OH)<sub>2</sub> is  $1.5 \times 10^{-3}$  M. Calculate the K<sub>sp</sub>. Answer - Write equilibrium equation

> Ratio -[] -Write equilibrium expression

2.) Given  $K_{sp}$  solve for solubility (either M or g/L)

<u>Ex.</u> -  $K_{sp}$  for  $CaCO_3 = 4.8 \times 10^{-9}$ . Calculate solubility in molarity.

<u>Answer</u> - Write equilibrium equation

Ratio -

[] -Write equilibrium expression

<u>Ex.</u> - Calculate the molar solubility of  $Pb(IO_3)_2$ .

<u>Answer</u> - Look up K<sub>sp</sub> for Pb(IO<sub>3</sub>)<sub>2</sub> on page 5 of data booklet. K<sub>sp</sub> = Write equilibrium equation Ratio -

[]-

Write equilibrium expression

- 3.) Trial K<sub>sp</sub> calculations. Just like K<sub>eq</sub> questions!!!!
  - If trial K<sub>sp</sub> > real K<sub>sp</sub>, then equilibrium shifts towards\_\_\_\_\_\_. In a solubility question, this means more \_\_\_\_\_\_ stuff = precipitate!!!
  - If trial  $K_{sp} < real K_{sp}$ , then equilibrium shifts towards \_\_\_\_\_ = more <u>dissolving</u>.
  - Ex. Will a precipitate form if 20.0 mL of 0.010 M CaCl2 are mixed with 20.0 mL of 0.0080 M Na2SO4?

$$(K_{sp} \ CaSO_4 = 2.45 \times 10^{-5})$$

Answer -

## Applications of Solubility

### Titration with Cl<sup>-</sup> Ions

- <u>Titration</u> -

- Titrations are undertaken to determine the [ ] of an unknown chemical.
- <u>Stoichiometric Point or Equivalence Point</u> point in a titration reaction where moles of reacting chemicals are the same ratio as in balanced equation.
- Let's look more closely at how a titration works using the following reaction:

 $Ag^{+} + Cl^{-} \rightarrow AgCl_{(s)}$  white ppt (precipitate)

 $K_{sp} AgCl = 1.8 \times 10^{-10}$ 

- If we have  $[Ag^+]$  of 0.10 *M* in solution then solving the K<sub>sp</sub> expression shows us the minimum  $[Ag^+]$  needed to form a precipitate with the Cl<sup>-</sup>.  $K_{sp} = [Ag^+][Cl^-]$   $1.8 \times 10^{-10} = [Ag^+][0.10]$   $[Ag^+] = 1.8 \times 10^{-9} M$ 

- How do we know when all Cl<sup>-</sup> is reacted?

- 1.) \_\_\_\_\_ (not very helpful as we can't really see this).
- 2.) Add CrO<sub>4</sub>-<sup>2</sup> ions (yellow) solution. Only adding 10% of solution as indicator

- When all the  $Cl^-$  is gone (reacted with silver ions), any addition  $Ag^+$  react with  $CrO_4^{-2}$ .

<mark>CrO₄<sup>-2</sup></mark> + Ag⁺ → <mark>Ag₂CrO₄ (red)</mark>

 $K_{sp} Ag_2CrO_4 = 1.1 \times 10^{-12}$   $K_{sp} = [Ag^+]^2[CrO_4^{-2}] 1.1 \times 10^{-12} = [Ag^+]^2[0.010]$   $[Ag^+] = 1.0 \times 10^{-5} M$ - As titration proceeds in the presence of both Cl<sup>-</sup> and CrO<sub>4</sub><sup>-2</sup> any Ag<sup>+</sup> is taken up by the Cl<sup>-</sup> (white ppt). When all the Cl<sup>-</sup> is gone, the next drop of Ag<sup>+</sup> will ppt as Ag<sub>2</sub>CrO<sub>4</sub> (red). This signals the end of titration.

\_\_\_\_\_= moles Ag⁺

Ex. - In order to find the [Cl<sup>-</sup>] in a sea water sample, a 25.0 mL sample was titrated with 0.500 M AgNO<sub>3</sub> solution, using sodium chromate as an indicator. At the equivalence point 26.8 mL of AgNO<sub>3</sub> solution had been added. What was the [Cl<sup>-</sup>] in the sea water sample?
Answer -

Ex. 2 - A 5.29 g sample of impure sodium chloride was dissolved and diluted to a total volume of 250.0 mL. If 25.0 mL of the sodium chloride solution required 28.5 mL of 0.300 M AgNO<sub>3</sub> solution to reach the equivalence point, using chromate indicator, what was the percentage purity of the original sodium chloride?
Answer -

### Hardness in Water

- "Hardness" in water is the presence of Ca<sup>+2</sup> and/or Mg<sup>+2</sup>. The calcium ions are often present from limestone deposits dissolving into the water (CaCO<sub>3</sub> + H<sup>+</sup>).
- The Ca<sup>+2</sup> (Mg<sup>+2</sup>) causes a bitter taste, white hard deposits when water has evaporated, and inhibits the action of the soap. The stearate ion (C<sub>17</sub>H<sub>35</sub>COO<sup>-</sup>) is the active ingredient of soap and is very insoluble with the Ca<sup>+2</sup> and Mg<sup>+2</sup> ions. This causes the soap to ppt a white "curd" causing more soap to be needed to do the actual cleaning.
   There are two types of "hard" water

 $\rightarrow$ 

 1.) \_\_\_\_\_\_ - Ca<sup>+2</sup> (Mg<sup>+2</sup>) with no natural HCO3<sup>-</sup>. You need washing soda (Na<sub>2</sub>CO<sub>3</sub>) to ppt Ca<sup>+2</sup> out. This is how your water softener works. ppt
 2.) \_\_\_\_\_\_ - Ca<sup>+2</sup> and natural HCO3<sup>-</sup>. Hardness can be removed by boiling! Ca<sup>+2</sup> + 2 HCO3<sup>-</sup> + energy → CaCO3 (s) + CO2 + H2O now soft!! - When dissolving a salt into **pure water** the solubility cannot be altered. However, if dissolving into not pure water then the solubility can be increased or decreased (not the solubility product (K<sub>sp</sub>)) by applying Le Chatelier's principle.

- In other words, when dissolving a salt like AgCl if there is already some Cl<sup>-</sup> in the solvent then less AgCl will be able to dissolve.

- Another way to look at this is from Le Chatelier's principle. If a saturated solution of AgCl has some AgNO<sub>3</sub> added there will be an increase in the Ag<sup>+</sup> from the AgNO<sub>3</sub>. The system will respond to counteract this addition of Ag<sup>+</sup>. This drives the equilibrium back towards the reactant or starting salt AgCl (thus decreasing the amount dissolved!).  $AgCl_{(s)} = \boxed{Ag^{+}_{(aq)}} + Cl^{-}_{(aq)}$ 

$$AgNO_{3}(s) \stackrel{\neg}{=} Ag^{*}(aq) + NO_{3}^{-}(aq)$$

- This lowering of the solubility by adding a salt with an ion in "common" is known as the \_\_\_\_\_

- Increasing the solubility of a salt is also possible. By adding a solution that will precipitate out one of the solutions ions the equilibrium will respond and drive the reaction towards the products or ions to counteract this addition.  $AgCl_{(s)} = \boxed{Ag^{+}_{(aq)}} + Cl^{-}_{(aq)}$ 

Add Na<sub>2</sub>S Na<sub>2</sub>S (s) 
$$\Leftrightarrow$$
  $S^{-2}$  (aq) + Na<sup>+</sup> (aq)  
 $\downarrow$   
Ag<sub>2</sub>S (s)

- So, what does a solubility calculation containing a common ion look like?

Ex. - What is the solubility of AgI in 0.25 M Nal?

Answer -

Part 1 - diss equil equation

Part 2 - K<sub>sp</sub> expression

Part 3 - Assumption!

Part 4 - Solve