

UNIT III: SOLUBILITY EQUILIBRIUM

I. Solutions: What are They?

Solution: a homogenous mixture of 2 or more pure substances. The pure substances can be of any state, gas with gas, solid with solid, solid with liquid, etc.

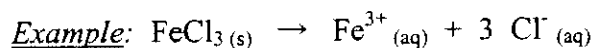
Example: Gas with gas solution: air
Solid with solid solution: alloy (mixture of metals)
Solid with liquid: salt solution

In Chem. 12, we are most interested in solutions containing a solid (salt), mixed with a liquid (H₂O).

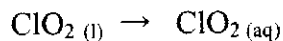
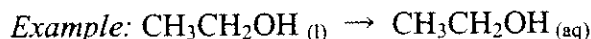
Solute: The solid that is dissolved in the liquid.
Solvent: the pure liquid in which the solute is dissolved.

A. Types of Aqueous Solutions:

1) Ionic Solutions: solution composed of a salt DISSOCIATING (ionizing) in water.



2) Molecular Solutions: solution composed of COVALENT compounds mixing with a solvent.



B. Saturated Solutions:

Saturated Solution: where the MAX amount of solute has been dissolved into the solvent. Extra solute added will simply sink to the bottom and not dissolve.

Characteristics of a Saturated Solution:

- There exists an EQUILIBRIUM between the dissolved and undissolved solute.
- Traces of undissolved solute are present at any given time.



The dissociation of AgBrO_3 is in equil^m with the recrystallization of the Ag^{+} and BrO_3^{-} ions back into solid AgBrO_3 .

II. Solubility of Salts:

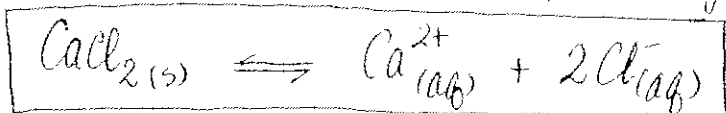
Solubility: the degree extent to which a solute can dissolve in a solvent at a given temperature. This value is usually expressed in molarity (M). Therefore, the solubility of a solute is the equil^m concentration of the solution.

Example: Solubility of $\text{AgBrO}_3 = 8.31 \times 10^{-3} \text{ M}$ - This means that a max. of 8.31×10^{-3} mol of AgBrO_3 solid can dissolve in 1L of H_2O . This system then attains equilibrium.

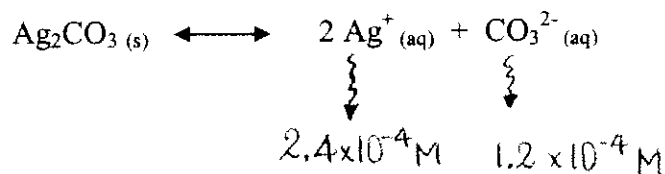
II. Calculating Solubility & Ion Concentrations:

Example: It is found that 250 mL of saturated CaCl_2 contains 18.6g of CaCl_2 at 20°C . What is the solubility of CaCl_2 ?

* implies system @ equilibrium.



Example: What is the [ion] of a saturated solution of Ag_2CO_3 with [] of $1.2 \times 10^{-4} \text{ M}$?



III. Determining the Extent of Solubility:

Some salts are completely soluble in water, meaning it will ionize completely in water, while other salts, when put into water, do not ionize as readily. These salts are said to have low solubility.

Example: $\text{NaCl}(s)$ has a solubility of $2.0 \times 10^1 \text{ M}$ (High solubility)

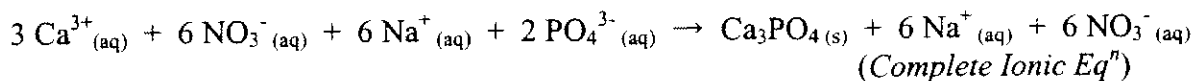
$\text{Ag}_2\text{CO}_3(s)$ has a solubility of $2.4 \times 10^{-4} \text{ M}$ (Low solubility)

A salt is said to have **low solubility** if a saturated solution has less than 0.1M of solute dissociated per 1L of solution. (This is an arbitrary value that has been set out by chemists).

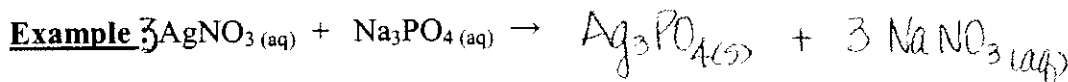
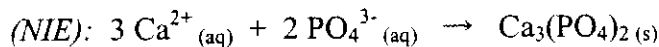
A. Predicting Solubility Qualitatively:

Some ions, when combined in solution, will undergo a reaction to form a PRECIPITATE.
 Precipitation can be predicted by looking at the "Solubility of Compounds" chart.
 Solutions which react to form a precipitate should be written with NET Ionic Equations (NIE).

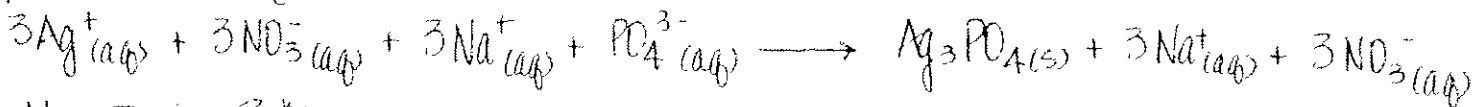
Example: $3 \text{Ca}(\text{NO}_3)_2(\text{aq}) + 2 \text{Na}_3\text{PO}_4(\text{aq}) \rightarrow \text{Ca}_3\text{PO}_4(\text{s}) + 6 \text{NaNO}_3(\text{aq})$ (Formula Equation)



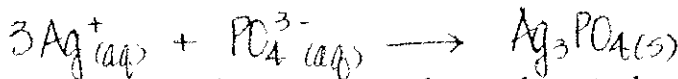
- **Spectator Ions:** those ions that did not change in state or phase from reactant to product.
- **Reacting Ions:** those ions that changed in state and underwent a chemical reaction from reactant to product. Only these ions are involved in the **Net Ionic Equation (NIE)**.



Complete Ionic Eqⁿ:



Net Ionic Eqⁿ:



- (i) **Qualitative Analysis:** using experimental procedures to determine which ion(s) are present in a solution.

Example: A solution Z contains one or more of Ag^{+} , Ba^{2+} , and Ni^{2+} . What ions could be added, and **in what order**, to determine which of these cations are present?

- Guidelines:** 1) Set up a table of solubilities. Refer to *Solubilities Chart*.
 2) Remember that you must only precipitate out **one** ion at a time.

	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.

Bad Choices: Because we want to ppt. out one ion @ a time, adding OH^{-} or PO_4^{3-} would not be appropriate as choices as they ppt. out all ions @ once.

Good Choices: * 1st step: Add $\text{NaCl}(\text{aq})$ * 2nd step: Add Na_2SO_4 or Na_2S .

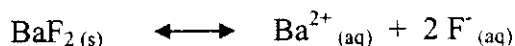
Example: A solution contains Sr^{2+} , Ca^{2+} , and Ag^+ . What compounds could be added, and in what order, to separate these ions?

- * 1st STEP: Add $\text{NaCl}_{(aq)}$ - This will ppt. out Ag^+ , if present.
- * 2nd STEP: Add $\text{NaOH}_{(aq)}$ - Will ppt. out Sr^{2+} , if present.
- * 3rd STEP: Add $\text{Na}_2\text{S}_{(aq)}$ - Will ppt. out Ca^{2+} , if present.

NOTE: Other answers can apply.

B. Quantitative Analysis of Solubility: K_{sp}

The dissociation of a solid salt in water always takes the following form:



$$K_{eq} = \frac{[\text{Ba}^{2+}][\text{F}^-]^2}{1}$$

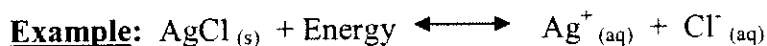
$$K_{sp} = [\text{Ba}^{2+}][\text{F}^-]^2$$

K_{sp} is simply a K_{eq} value, but for ionic salt solutions.

K_{sp} : **Solubility Product Constant** – shows quantitatively the extent to which a saturated salt solⁿ dissociates.

NOTE:

- The dissociation of insoluble salts are always endothermic.
- Salts with limited solubility attain equil^m due to competing entropy and enthalpy factors.
- Therefore, only insoluble salts can have a K_{sp} value.



ΔS : favours products
 ΔH : favours reactants

Therefore, equil^m at saturation point.

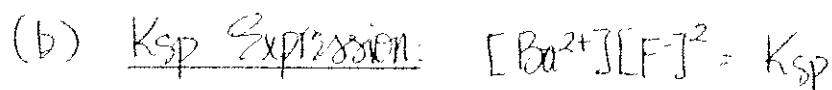
- a) High K_{sp} : favours products – High solubility – Salt dissociates readily into ions
- b) Low K_{sp} : favours reactants – Low solubility – Salt does not dissociate readily.

Example: AgCl : $K_{sp} = 1.8 \times 10^{-10}$
 AgI : $K_{sp} = 8.5 \times 10^{-17}$ □ AgCl is more soluble than AgI .

Solving K_{sp} Problems:

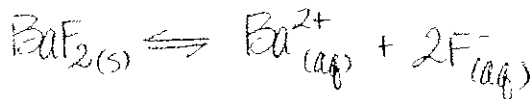
1. Concentration given, find K_{sp} value

Example: A solⁿ of BaF_2 in equil^m contains $4.59 \times 10^{-2} M Ba^{2+}$ and $2.00 \times 10^{-3} M F^-$. What is the K_{sp} for BaF_2 ?



(c) $(4.59 \times 10^{-2} M)(2.00 \times 10^{-3} M)^2 = 1.84 \times 10^{-7}$

Example: A saturated solⁿ of BaF_2 contains 3.58×10^{-3} mol of BaF_2 in a 3.00L solⁿ. What is the K_{sp} for BaF_2 ?



$$K_{sp} = [Ba^{2+}][F^-]^2$$

* Solubility of BaF_2 : $\frac{3.58 \times 10^{-3} \text{ mol}}{3.00 \text{ L}} = 0.001193 M$

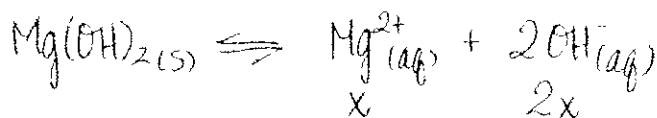
$[Ba^{2+}] = 0.001193 M$
 $[F^-] = 0.002386 M$

$$K_{sp} = (0.002386)^2 (0.001193) = 6.8 \times 10^{-9}$$

2. K_{sp} value given, find [ions]

Example: What is the $[Mg^{2+}]$ in a saturated solⁿ of $Mg(OH)_2$?

* Look in Data Booklet for K_{sp} of $Mg(OH)_2$: 5.6×10^{-12}



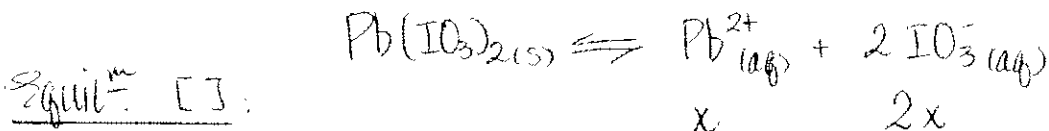
$$K_{sp} = [Mg^{2+}][OH^-]^2$$

$$5.6 \times 10^{-12} = (x)(2x)^2$$

$$* 5.6 \times 10^{-12} = 4x^3$$

$$* x = 1.12 \times 10^{-4} = [Mg^{2+}]$$

Example: What mass of Pb^{2+} is present in 5.0 L of saturated $\text{Pb}(\text{IO}_3)_2$? $K_{sp} = 3.7 \times 10^{-13}$



$$K_{sp} = [\text{Pb}^{2+}][\text{IO}_3^-]^2$$

$$3.7 \times 10^{-13} = (x)(2x)^2$$

$$* x = 4.5 \times 10^{-5} \text{ M}$$

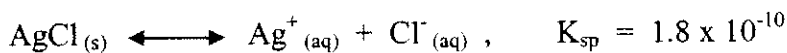
$$* 4.5 \times 10^{-5} \text{ M} \times 5.0 \text{ L} = 2.26 \times 10^{-4} \text{ mol}$$

$$* 2.26 \times 10^{-4} \text{ mol Pb}^{2+} \times \frac{207.2 \text{ g}}{\text{mol}} = 0.047 \text{ g}$$

3. Predicting whether a Precipitate will Form: Trial Ion Product (TIP)

- a) $\text{TIP} > K_{sp}$ = a ppt. will form.
- b) $\text{TIP} < K_{sp}$ = a ppt. won't form
- c) $\text{TIP} = K_{sp}$ = a completely saturated solⁿ is formed

Example: Will a ppt. form when 5.0 mL of $6.0 \times 10^{-5} \text{ M Ag}^+$ mixes with 10.0 mL of $4.2 \times 10^{-6} \text{ M Cl}^-$?



$$[\text{Ag}^+]_{\text{final}} = (6.0 \times 10^{-5} \text{ M})(0.0050 \text{ L}) = M_f(0.015 \text{ L})$$

$$M_f = 2 \times 10^{-5} \text{ M}$$

$$[\text{Cl}^-]_{\text{final}} = (4.2 \times 10^{-6} \text{ M})(0.010 \text{ L}) = M_f(0.015 \text{ L})$$

$$M_f = 2.8 \times 10^{-6} \text{ M}$$

$$* \text{TIP} = (2 \times 10^{-5})(2.8 \times 10^{-6})$$

$$= 5.6 \times 10^{-11}$$

* $\text{TIP} < K_{sp}$: no ppt.

Example: If 25.0 mL of $4.50 \times 10^{-3} \text{ M Pb}(\text{NO}_3)_2$ is mixed with 35.0 mL of $2.80 \times 10^{-3} \text{ M MgI}_2$, will a ppt. form?

Find the NIE for rxn. between the two solutions:

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

$$[\text{Pb}^{2+}]_f = (4.50 \times 10^{-3} \text{ M})(0.025 \text{ L}) = M_f(0.060 \text{ L})$$

$$M_f = 0.001875 \text{ M}$$

$$[\text{I}^-]_f = (2.80 \times 10^{-3} \text{ M})(0.035 \text{ L}) = M_f(0.060 \text{ L})$$

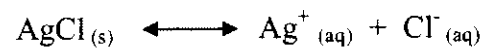
$$M_f = 0.00163 \text{ M} \times 2 = 0.00327 \text{ M}$$

$$K_{sp} = (0.001875 \text{ M})(0.00327 \text{ M})^2 = 2 \times 10^{-8}$$

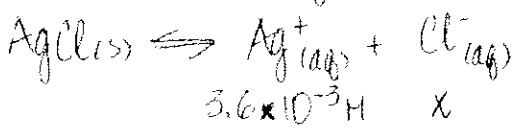
* $\text{TIP} > K_{sp}$: ppt. forms

* means right @ saturation pt.

Example: What [Cl⁻] is required to just start pptn of AgCl from a 3.6 x 10⁻³M solution of Ag⁺?



* Understanding the Question: (a) You have a 3.6 x 10⁻³M Ag⁺ solⁿ in beaker A.



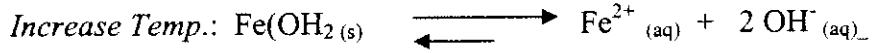
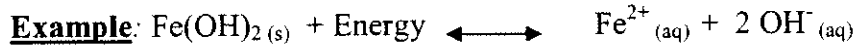
(b) You will add an amount of Cl⁻ from beaker B - of which you do not know the []

$$1.8 \times 10^{-10} = (3.6 \times 10^{-3} \text{M})(x)$$

IV. Altering the Solubility of a Salt:

A. Changing the Temperature:

- Insoluble salts dissociate *endothermically*. Therefore, to increase solubility, we should heat the of the solution.

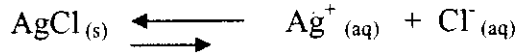


B. The Common Ion Effect:

Common Ion Effect: Decreasing the solubility of a salt by adding a second salt which has one ion **IN COMMON** with the first salt.

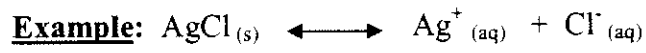


- Decrease Solubility by:
- Adding AgNO₃(aq)
 - Adding NaCl(aq)

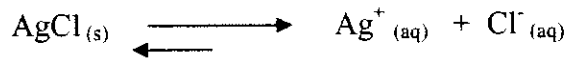


C. Increasing the Solubility by Precipitation:

If we can precipitate out one of the ions in a dissociation equation, Le Chatelier's Principle would force the equil^m towards the product side, thus increasing solubility.



- Increase Solubility by:
- Adding Na₂SO₄(aq)
 - Adding Pb(NO₃)₂(aq)



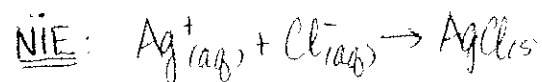
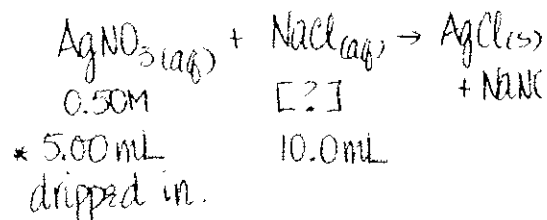
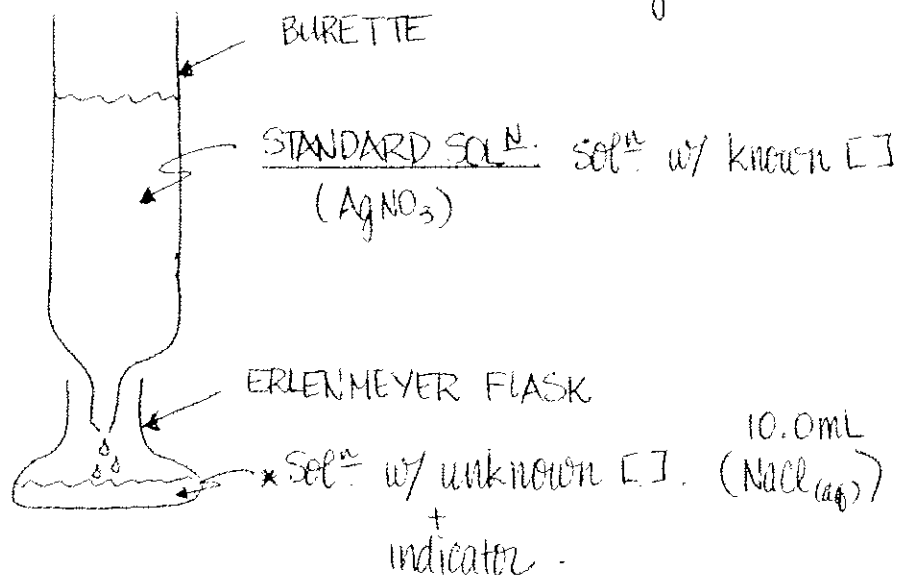
V. Applications of Solubility Principles:

A. Chloride Titrations:

Titration: a lab technique performed to determine the unknown [] of a solution. A standard solution, whose [] is known, is reacted with the unknown until **equivalence point** is reached.

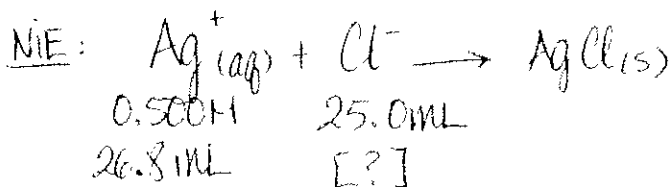
Equivalence Point: the point in the titration where the mole ratio in the reacting vessel exactly match the ratio in the balanced equation.

An indicator is used to "visually" cue the end point of the titration.



* In the case of a precipitation titration, the very first appearance of a solid in the Erlenmeyer flask is a cue that rxn. is complete.

Example: In order to find [Cl⁻] in a sea water sample, a 25.0mL sample was titrated with 0.500M AgNO₃ solution. At the equiv. point, 26.8mL of AgNO₃ has been added. What is the [Cl⁻]?

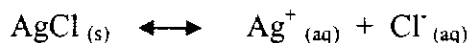


$$* (0.500\text{M})(0.0268\text{L}) = 0.0134 \text{ mol Ag}^+$$

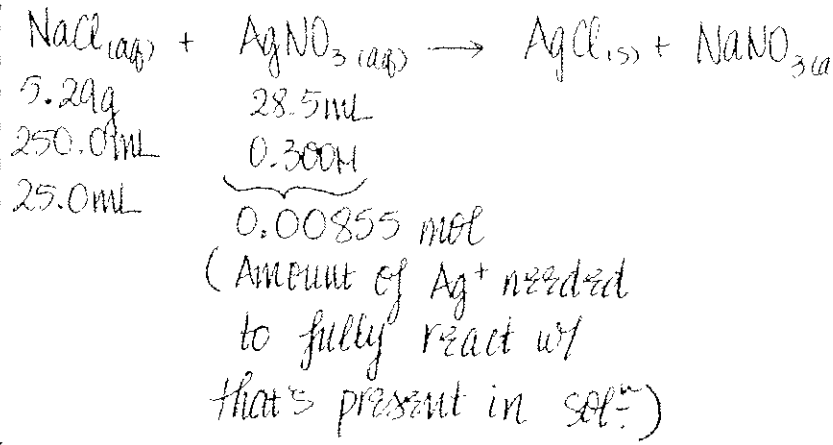
$$* 0.0134 \text{ mol Ag}^+ \times \frac{1 \text{ Cl}^-}{1 \text{ Ag}^+} = 0.0134 \text{ mol Cl}^- \text{ (was originally in the sample).}$$

$$* \frac{0.0134 \text{ mol Cl}^-}{0.0250\text{L}} = 0.536\text{M} = [\text{Cl}^-]$$

Example: A 5.29g of **impure** NaCl was dissolved and diluted to a total volume of 250.0mL. If 25.0 mL of the sodium chloride solution required 28.5mL of 0.300M AgNO₃ solution to reach equiv. point., using chromate as indicator, what was the % purity of the original NaCl?

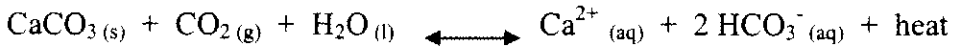
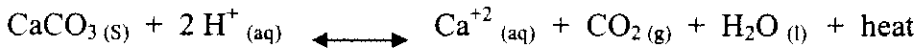


* $0.00855 \text{ mol Ag}^+ \times \frac{1 \text{ Cl}^-}{1 \text{ Ag}^+} = 0.00855 \text{ mol Cl}^-$



B. Removing Pollution & Hardness from H₂O

- "Hardness" in water results from presence of Ca²⁺ and Mg²⁺.
- Ca²⁺ results from the acid induced dissociation of naturally occurring limestone (CaCO₃).
- Mg²⁺ result from the acid induced dissociation of MgCO₃ found in all rocks.



How to Remove Water Hardness:

Problem	Solution
1) Hard water tastes bitter due to dissolved Mg ²⁺ and Ca ²⁺	If the hard water contains HCO ₃ ⁻ , then <u>heat</u> the water. Then remove the solid CaCO ₃ by <u>filtering</u> . (Temporary Hard Water)
2) Soaps do not work effectively – The active ion in soap is stearate (C ₁₇ H ₃₅ COO ⁻). This ion ppts with Ca ²⁺ and Mg ²⁺ .	Carry out a pptn rxn. to remove the Ca ²⁺ or Mg ²⁺ from the water. If water does not have HCO ₃ ⁻ ion – This is considered <u>permanent</u> hard water.

* TEMPORARY HARD H₂O Gets its name from the fact that after heating the solⁿ, the equil^m shifts left, The CaCO_{3(s)} can be filtered off, the CO_{2(g)} dissipates, giving you back pure H₂O_(l).

