

## Solubility and Solubility Equilibrium: Student Review Notes

A **solution** is a homogeneous mixture of a solute distributed through a solvent

Solutions can exist in any phase  
substance being dissolved                      substance doing the dissolving

- gas -- air is a good example. It's a mixture of oxygen, nitrogen and other gases.
- liquid -- the ocean is a good example of a saline solution.
- solid -- metal alloys such as bronze (Cu, Zn & Sn).

**Unsaturated** - a solution that contains a smaller amount of solute than the solubility at the given temperature

**Saturated** - a solution that is in equilibrium with undissolved solute at a given temperature. The concentration of solute in a saturated solution is called the **solubility** of the solute.

**Supersaturated** - an unstable condition in which the solution contains more than the equilibrium amount of solute at the given temperature.

### Principles of Solubility

The extent to which a solute dissolves in a solvent depends on several factors:

- 1) Solute and solvent interactions
- 2) Temperature
- 3) Pressure

### Solute and Solvent Interactions

The golden rule  
 "Like Dissolves Like"

two substances with similar intermolecular forces will be soluble or miscible with each other

<u>Solute</u>	<u>Solvent</u>	<u>Solute-Solute IMF</u>	<u>Solvent-Solvent IMF</u>	<u>Solute-Solvent IMF</u>	<u>Solution Forms</u>
ethyl alcohol	water	H-bonding	H-bonding	H-bonding	yes
I <sub>2</sub>	water	dispersion	H-bonding	dispersion	no
I <sub>2</sub>	CCl <sub>4</sub>	dispersion	dispersion	dispersion	yes

### Effect of Temperature on Solubility

**Solids** are more soluble at higher temperatures: Solid + Liquid + Heat  $\longrightarrow$  Solution

|  
 heat must be absorbed to break down  
 the crystal lattice. Ex, sugar in hot tea vs. ice tea

**Gases** are less soluble at higher temperatures: Gas + Liquid  $\longrightarrow$  Solution + Heat

|  
 dissolving a gas evolves heat since the gas must be condensed.  
 A good example is soda.

### Effect of Pressure on Solubility

At given temperature, an increase in pressure will increase the solubility of a gas. This is why when you open a can of soda (decrease the pressure) the its fizzes (the gas is less soluble in the solution and comes out of it)

### Insoluble Molecules

This sounds like a contradiction but solubility equilibrium is about the dissolution of insoluble species in water. The term insoluble doesn't mean that nothing dissolves. Rather, it means that only a small amount of the solute can be supported in solution by the solvent.

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## Solubility Rules

First things first, you have to **memorize the basic solubility rules** in order to (1) know which salts dissociate (break apart) in solution and (2) which ions combine to form precipitates when you mix solutions. The other part of this is that if you are given the name of a compound, you have to know the associated chemical formula. This means that it is assumed that you've memorized most of the standard polyatomic ions.

Here are the general rules for things that are **SOLUBLE in Water** (there are exceptions but if you remember these, you'll be able to predict if a salt is soluble most of the time):

- All salts comprised from alkali metals (Group I), nitrate ( $\text{NO}_3^-$ ), and ammonium ( $\text{NH}_4^+$ ), chlorate ( $\text{ClO}_3^-$ ), and bicarbonate ( $\text{HCO}_3^-$ ) are soluble in water. It doesn't matter what the other anion or cation is in the salt. So get that, you cannot form a precipitate by combining a cation or anion with any of these ions. Repeat the rules to yourself:
  - All Group I metal salts are soluble
  - All nitrates are ( $\text{NO}_3^-$ ) soluble
  - All ammonium ( $\text{NH}_4^+$ ) salts are soluble
  - All chlorates ( $\text{ClO}_3^-$ ) are soluble
  - All bicarbonates ( $\text{HCO}_3^-$ ) are soluble
- Almost all sulfates ( $\text{SO}_4^{2-}$ ) are soluble, except  $\text{BaSO}_4$ ,  $\text{CaSO}_4$ ,  $\text{PbSO}_4$ ,  $\text{HgSO}_4$ , and  $\text{Ag}_2\text{SO}_4$ .
- Almost all chlorides, iodides, bromides, and fluorides are soluble, except precipitates containing mercury(I) ( $\text{Hg}_2^{2+}$ , not  $\text{Hg}^{2+}$ !!),  $\text{Pb}^{2+}$ , or  $\text{Ag}^+$ .

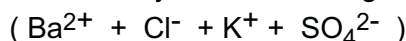
Here are the general rules for things that are **INSOLUBLE in Water** (again, there are exceptions but if you remember these, you'll be able to predict if a salt is insoluble most of the time):

- All salts comprised from Phosphates ( $\text{PO}_4^{3-}$ ), chromates ( $\text{CrO}_4^{2-}$ ), carbonates ( $\text{CO}_3^{2-}$ ), sulfides ( $\text{S}^{2-}$ ) and sulfites ( $\text{SO}_3^{2-}$ ) are insoluble with everything **except the cations listed above** (Group I metals and ammonium). Hydroxides ( $\text{OH}^-$ ) are also insoluble although  $\text{Ba}(\text{OH})_2$  is somewhat soluble.

Let's do the same drill, repeat these rules to yourself

- All Phosphates ( $\text{PO}_4^{3-}$ ) are insoluble except for Group I metal and ammonium salts
- All chromates ( $\text{CrO}_4^{2-}$ ) are insoluble except for Group I metal and ammonium salts
- All carbonates ( $\text{CO}_3^{2-}$ ) are insoluble except for Group I metal and ammonium salts
- All sulfides ( $\text{S}^{2-}$ ) are insoluble except for Group I metal and ammonium salts

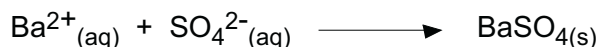
For example: Mix together aqueous solutions of barium chloride ( $\text{BaCl}_2$ ) and potassium sulfate ( $\text{K}_2\text{SO}_4$ ). Both of these are soluble in water, so before you mix them together what you've really got is:



To check and see if a precipitate will form, switch ions and check the solubility rules:

$\text{BaSO}_4$  is insoluble and that's a big yes to a precipitate (ppt).  $\text{KCl}$  is soluble, so no ppt.

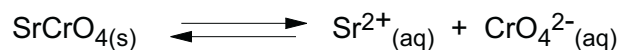
When you write out the overall rxn, make sure you write out the net ionic equation (only include ions that do something, spectator ions algebraically cancel out). For the example, the net ionic equation would be:



**Solubility and Solubility Equilibrium: Student Review Notes**

Now, equilibrium is this idea of reversibility in chemical reactions. It might seem kind of oxymoronic to talk about equilibrium for insoluble species, but we can talk about equilibrium of insoluble molecules because, to some small extent, all insoluble products dissolve in solution and reach an equilibrium. Everything dissolves in everything and there's a little bit of everything, everywhere. A little bit can be a very little bit though. The **equilibrium constant for the dissolution of insoluble/slightly soluble molecules is called the solubility product constant,  $K_{sp}$**

For example: put some strontium chromate into water



$$\text{Solubility Product Constant, } K_{sp} = [\text{Sr}^{2+}][\text{CrO}_4^{2-}] = (\text{s})(\text{s}) = \text{s}^2$$

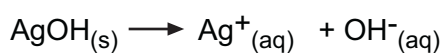
you can use molar concentration or solubility, s, as the variable

**Get comfortable using molar concentration or solubility as the variable in these problems.**

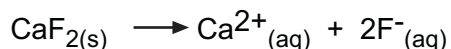
If a solution is saturated, s = solubility = the concentration of the insoluble species ( the solid) in solution. Use the stoichiometry of the equation to get the concentration of the ions or right the expression in terms of solubility to calculate a value for  $K_{sp}$

**Don't just use the magnitude of  $K_{sp}$  to determine if one species is more or less soluble than another**

For example, given the following information, who is more soluble, AgOH or CaF<sub>2</sub>?



$$K_{sp} = 1.5 \times 10^{-8}$$



$$K_{sp} = 4.0 \times 10^{-11}$$

**DON'T**

Just jump to the conclusion that the most soluble species is the one with the larger  $K_{sp}$

You have to look at how solubility, s, is used in the  $K_{sp}$  expression:

$$\text{AgOH: } K_{sp} = [\text{Ag}^+][\text{OH}^-] = (\text{s})(\text{s}) = \text{s}^2 = 1.5 \times 10^{-8} \quad \text{solubility, } \text{s} = 1.2 \times 10^{-4} \text{ M}$$

$$\text{CaF}_2: K_{sp} = [\text{Ca}^{2+}][\text{F}^-]^2 = (\text{s})(2\text{s})^2 = 4\text{s}^3 = 4.0 \times 10^{-11} \quad \text{solubility, } \text{s} = 2.2 \times 10^{-4} \text{ M}$$

Basic  $K_{sp}$  problems you need to know how to solve

**1. Given the value of  $K_{sp}$ , calculate the solubility and the concentration of the cation and anion**

$$\text{Ag}_2\text{CO}_3: K_{sp} = 8.1 \times 10^{-12} \quad \text{what is the solubility?}$$

$$K_{sp} = [\text{Ag}^+]^2 [\text{CO}_3^{2-}] = (2\text{s})^2(\text{s}) = 4\text{s}^3$$

$$\text{s} = 1.3 \times 10^{-4} \text{ M}$$

$$[\text{Ag}^+] = 2\text{s} = 2.6 \times 10^{-4} \text{ M}$$

$$[\text{CO}_3^{2-}] = \text{s} = 1.3 \times 10^{-4} \text{ M}$$

**2. Given the concentration of the insoluble species in a saturated solution, calculate  $K_{sp}$** 

In a saturated solution of barium carbonate, the concentration of BaCO<sub>3</sub> = 8.94 x 10<sup>-5</sup> M

What is the solubility product constant,  $K_{sp}$  for BaCO<sub>3</sub>?

$$K_{sp} = [\text{Ba}^{2+}][\text{CO}_3^{2-}] = (\text{s})(\text{s}) = \text{s}^2 = (8.94 \times 10^{-5})^2 = 8.0 \times 10^{-9}$$

**Solubility and Solubility Equilibrium: Student Review Notes**

Basic  $K_{sp}$  problems you need to know how to solve, continued.

**3. Calculate the concentration of ions in solution**

$Pb^{2+}$  and  $Cl^-$  solutions are mixed and a ppt forms. If  $[Cl^-] = .1M$ , what is the concentration of  $Pb^{2+}$ ?

$$PbCl_2: K_{sp} = 1.7 \times 10^{-5}$$

$$K_{sp} = [Pb^{2+}] [Cl^-]^2 = [Pb^{2+}](.1)$$

$$[Pb^{2+}] = 1.7 \times 10^{-3} M$$

**4. You can be asked to tell whether or not a ppt will form when two solutions are mixed.**

use a  $Q_{sp}$  and compare it to  $K_{sp}$ :

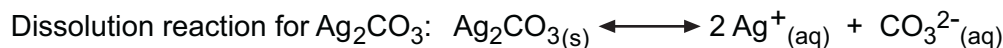
$$Q_{sp} > K_{sp} \text{ ppt forms}$$

$$Q_{sp} < K_{sp} \text{ no ppt}$$

$$Q_{sp} = K_{sp} \text{ is saturated to the point of precipitation, anything more will produce the first ppt.}$$

For example: Will a ppt form when 75 ml of 0.02 M  $Ag_2SO_4$  is mixed with 50 ml of 0.005M  $K_2CO_3$ ?

$$\text{The } K_{sp} \text{ of } Ag_2CO_3 = 8 \times 10^{-12}$$



Okay, the trickiest thing is to remember to add the individual solution volumes and calculate a molarity for each ion in the mixture.

$$\text{Total Volume} = .075L + .05L = .125L$$

$$\text{moles } Ag^+ = (2)(.02M)(.075L) = .003 \text{ moles}$$

$$[Ag^+] = .003\text{moles}/.125L = .024 M$$

$$\text{moles } CO_3^{2-} = (.005M)(.05L) = .00025 \text{ moles}$$

$$[CO_3^{2-}] = .00025\text{moles}/.125L = .002 M$$

$$Q_{sp} = [CO_3^{2-}][Ag^+]^2 = (.002M)(.024)^2 = 1.2 \times 10^{-6} > K_{sp} \quad \text{yes it will precipitate}$$

**5. The Common Ion Effect**

The value of the solubility product constant,  $K_{sp}$  is a function of temperature so it can change but at a given temperature, the equilibrium expression must be satisfied and this is where the introduction of an ion common to the insoluble species affects solubility. This is not a difficult idea to understand. All you need to do is careful bookkeeping for each of the species in solution. Take a look.

$$Ag_2CO_3: K_{sp} = 8.1 \times 10^{-12} \text{ what is the solubility?}$$

$$K_{sp} = [Ag^+]^2 [CO_3^{2-}] = (2s)^2(s) = 4s^3$$

$$s = 1.3 \times 10^{-4} M$$

Solid  $Ag_2CO_3$  is dumped into a .1 M solution of sodium carbonate  $Na_2CO_3$ .

What is the solubility of silver carbonate.

Well, we know that sodium carbonate is soluble--all Group I metal salts are soluble.

Therefore it has completely dissociated and the concentration of  $CO_3^{2-}$  is .1 M.

Do the equilibrium:

$$Ag_2CO_3: K_{sp} = 8.1 \times 10^{-12}$$

$$K_{sp} = [Ag^+]^2 [CO_3^{2-}] = (2s)^2(.1 + s)$$

carbonate ion in solution  
It's also a good assumption that  $s \ll .1$   
and therefore  $(.1 + s) \sim .1$

$$K_{sp} = .4s^2 = 8.1 \times 10^{-12}$$

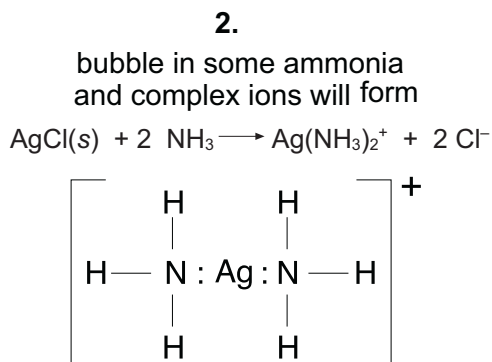
$$s = 4.5 \times 10^{-6} M \leftarrow \text{the presence of the common ion has decreased the solubility from } 1.3 \times 10^{-4} M$$

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There's another reaction that can occur in water that involves the formation of complex ions. Complex ions occur when a metal atom is joined by a coordinate covalent bond to neutral molecules and/or ions. For a complex ion, the **metal** is in the center and the species that bonds to it with coordinate covalent bond are called a **ligands**.

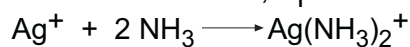
This comes into play regarding solubility because it's a way of making insoluble compounds dissolve in solution. It happens like this:

1.  
put AgCl into H<sub>2</sub>O  
It's insoluble  
so it just sits  
as a ppt.



3.  
Now look at the equilibrium of  
the complex ion

The name of the equilibrium  
constant for this is the  
formation constant,  $K_f$



$$K_f = \frac{[\text{Ag(NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2} = 1.7 \times 10^7$$

Formation of the complex ion is highly favorable based on the value of the formation constant.

The Cl precipitate disappears because all the Ag<sup>+</sup> keeps getting used up in the formation of the complex ion and remember that the  $K_{sp}$  for AgCl still must be satisfied. If the  $[\text{Ag}^+]$  term in  $[\text{Ag}^+][\text{Cl}^-]$  keeps going to zero and the product has to be a finite number, AgCl will keep dissolving back into solution.

Here are some common examples and the complex ions that you should know:

- |   |  |
|---|--|
| A. Ammine Complexes                                     |  |
| 2. Silver Chloride:                                     | $\text{AgCl}_{(s)} + 2 \text{NH}_3 \longrightarrow \text{Ag(NH}_3)_2^+ + 2 \text{Cl}^-$                              |
| 6. Zinc Hydroxide:                                      | $\text{Zn(OH)}_{2(s)} + 4 \text{NH}_3 \longrightarrow \text{Zn(NH}_3)_4^{2+} + 2 \text{OH}^-$                        |
| B. Cyanide Complexes                                    |  |
| 2. Silver cyanide:                                      | $\text{AgCN}_{(s)} + \text{CN}^- \longrightarrow \text{Ag(CN)}_2^-$  |
| 4. Copper(I) cyanide:                                   | $\text{CuCN}_{(s)} + \text{CN}^- \longrightarrow \text{Cu(CN)}_2^-$  |
| C. Hydroxide Complexes (mixed with a concentrated base) |  |
| 1. Aluminum Hydroxide:                                  | $\text{Al(OH)}_{3(s)} + \text{OH}^- \longrightarrow \text{Al(OH)}_4^-$   |
| 2. Aluminum oxide:                                      | $\text{Al}_2\text{O}_{3(s)} + \text{OH}^- \longrightarrow \text{Al(OH)}_4^-$ (not balanced... water also a reactant) |
| 3. Zinc Hydroxide:                                      | $\text{Zn(OH)}_{2(s)} + 2 \text{OH}^- \longrightarrow \text{Zn(OH)}_4^{2-}$  |
| D. Aqua Complexes                                       |  |
| 1. Aluminum:  | $\text{Al(NO}_3)_3(s) + 6 \text{H}_2\text{O} \longrightarrow \text{Al(H}_2\text{O)}_6^{3+} + 3 \text{NO}_3^-$        |
| 2. Iron(III):   | $\text{Fe(NO}_3)_3(s) + 6 \text{H}_2\text{O} \longrightarrow \text{Fe(H}_2\text{O)}_6^{3+} + 3 \text{NO}_3^-$        |