Solubility Equilibria

Chem 30S Review…Solubility Rules

- Salts are generally more soluble in HOT water(Gases are more soluble in COLD water)
- Alkali Metal salts are very soluble in water.

$NaCl$, KOH, Li_3PO_4, Na_2SO_4 etc...

- Ammonium salts are very soluble in water.

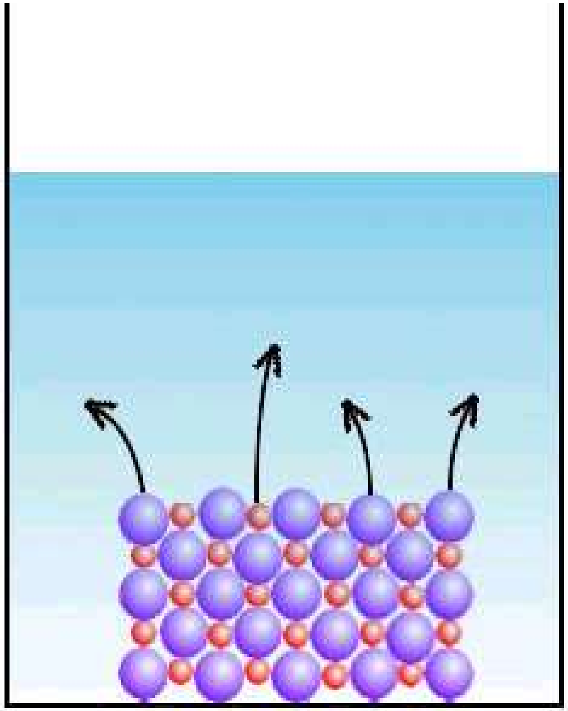
NH_4Br, $(NH_4)_2CO_3$ etc…

- Salts containing the nitrate ion, NO_3^-, are very soluble in water.
- Most salts of Cl^-, Br^- and I^- are very soluble in water - exceptions are salts containing Ag^+ and Pb^{2+}.

soluble salts: $FeCl_2$, $AlBr_3$, MgI_2 etc...

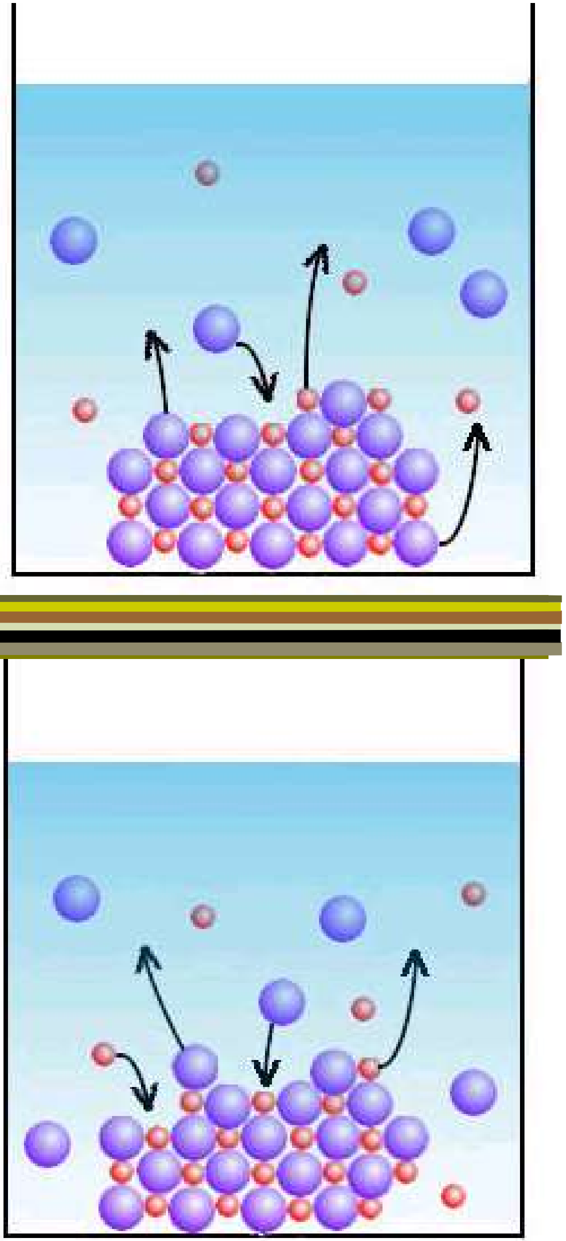
“insoluble” salts: $AgCl$, $PbBr_2$ etc...

Dissolving a salt...



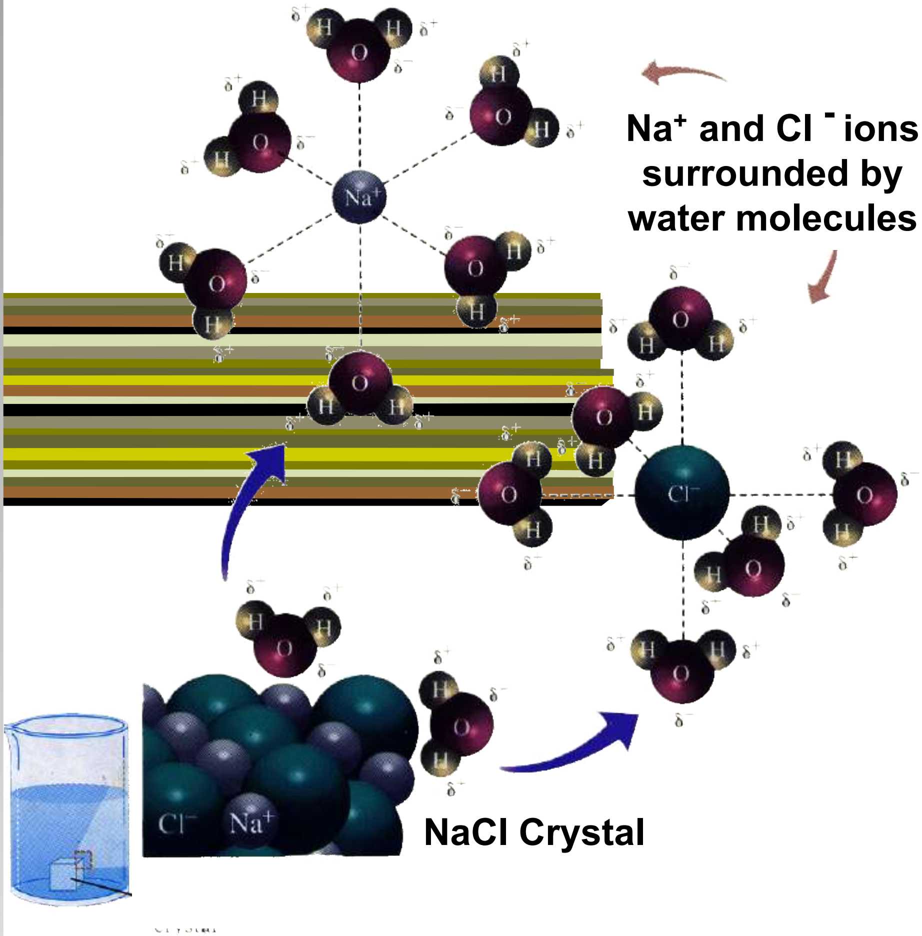
Salt is initially put into the water and begins dissolving.

- A salt is an ionic compound - usually a metal cation bonded to a non-metal anion.
- The dissolving of a salt is an example of equilibrium.
- The cations and anions are attracted to each other in the salt.
- They are also attracted to the water molecules.
- The water molecules will start to pull out some of the ions from the salt crystal.



- At first, the only process occurring is the dissolving of the salt - the **dissociation** of the salt into its ions.
- However, soon the ions floating in the water begin to collide with the salt crystal and are “pulled back in” to the salt. (**precipitation**)
- Eventually the rate of dissociation is equal to the rate of precipitation.
- The solution is now “**saturated**”. It has reached **equilibrium**.

Solubility Equilibrium: Dissociation = Precipitation



Na^+ and Cl^- ions surrounded by water molecules

NaCl Crystal

Dissolving NaCl in water

In a <u>saturated</u> solution, there is no change in amount of solid precipitate at the bottom of the beaker.

Concentration of the solution is constant.

The rate at which the salt is dissolving into solution equals the rate of precipitation.

Dissolving silver sulfate, Ag_2SO_4, in water

- When silver sulfate dissolves it dissociates into ions. When the solution is saturated, the following equilibrium exists:

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

- Since this is an equilibrium, we can write an equilibrium expression for the reaction:

$$Ksp = [Ag^+]^2[SO_4^{2-}]$$

Notice that the Ag_2SO_4 is left out of the expression! Why?

Since K is always calculated by just multiplying concentrations, it is called a "*solubility product*" constant - Ksp.

Writing solubility product expressions...

- For each salt below, write a balanced equation showing its dissociation in water.
- Then write the Ksp expression for the salt.

Iron (III) hydroxide, $Fe(OH)_3$

Nickel sulfide, NiS

Silver chromate, Ag_2CrO_4

Zinc carbonate, $ZnCO_3$

Calcium fluoride, CaF_2

Try Problems 1 - 8

Some K_{sp} Values

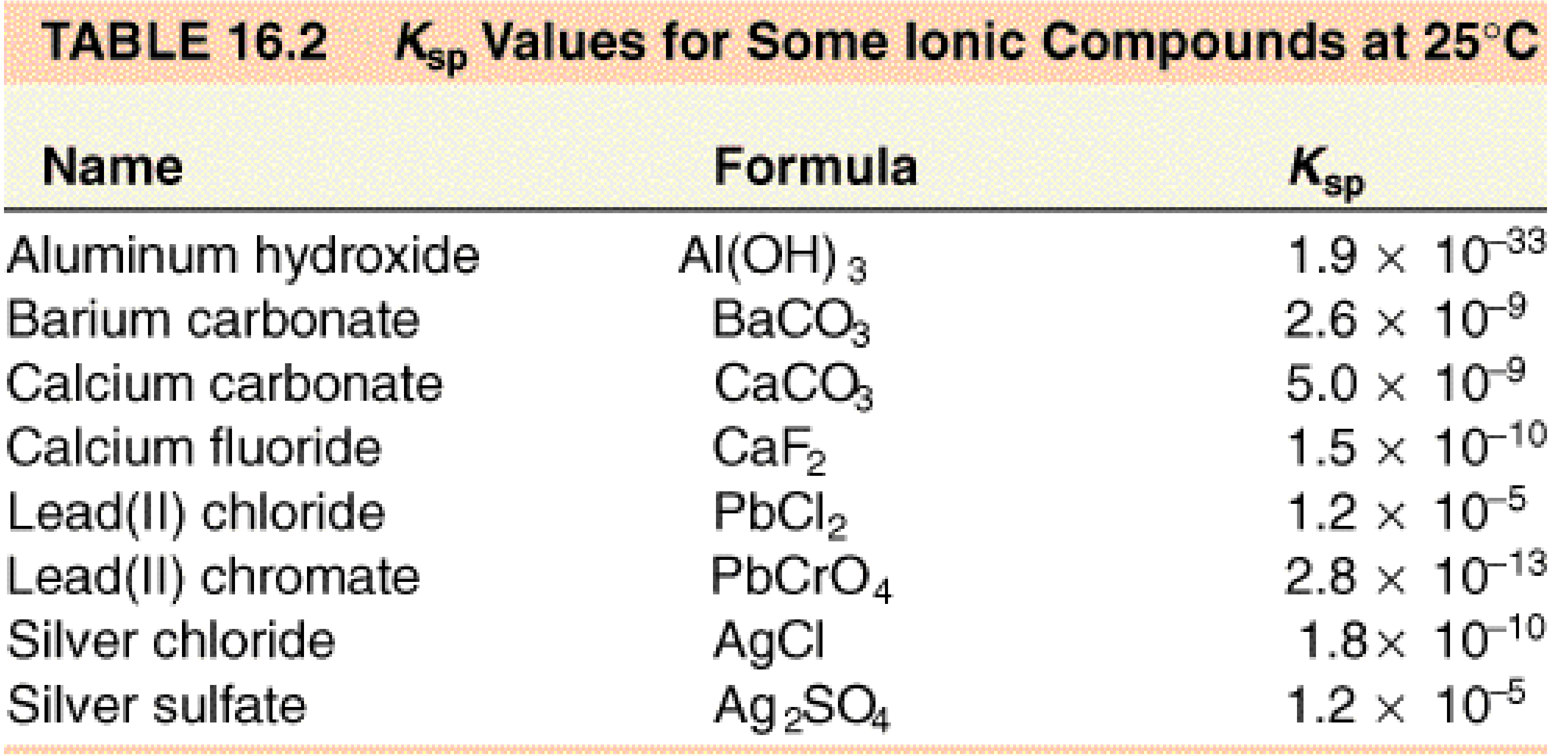


TABLE 16.2 K_{sp} **Values for Some Ionic Compounds at 25°C**

Name	Formula	K_{sp}
Aluminum hydroxide	$Al(OH)_3$	1.9×10^{-33}
Barium carbonate	$BaCO_3$	2.6×10^{-9}
Calcium carbonate	$CaCO_3$	5.0×10^{-9}
Calcium fluoride	CaF_2	1.5×10^{-10}
Lead(II) chloride	$PbCl_2$	1.2×10^{-5}
Lead(II) chromate	$PbCrO_4$	2.8×10^{-13}
Silver chloride	$AgCl$	1.8×10^{-10}
Silver sulfate	Ag_2SO_4	1.2×10^{-5}

Note:
These are experimentally determined, and may be slightly different on a different Ksp table.

Calculating K_{sp} of Silver Chromate

- A saturated solution of silver chromate, Ag_2CrO_4, has $[Ag^+] = 1.3 \times 10^{-4}$ M. What is the K_{sp} for Ag_2CrO_4?

$$Ag_2CrO_{4\,(s)} \leftrightarrows 2\,Ag^+_{(aq)} + CrO_4^{2-}{}_{(aq)}$$

1.3×10^{-4} M

$$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$$

$$K_{sp} = (1.3 \times 10^{-4})^2\,(6.5 \times 10^{-5}) = \mathbf{1.1 \times 10^{-12}}$$

Calculating the Ksp of silver sulfate

- The solubility of silver sulfate is 0.014 mol/L. This means that 0.0144 mol of Ag_2SO_4 will dissolve to make 1.0 L of saturated solution. Calculate the value of the equilibrium constant, Ksp for this salt.

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

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+ 2s + s

2s s

$$K_{sp} = [Ag^+]^2[SO_4^{2-}] = (2s)^2(s) = (4s^2)(s) = 4s^3$$

We know: s = 0.0144 mol/L

$$K_{sp} = 4(0.0144)^3 = 1.2 \times 10^{-5}$$

Calculating solubility, given Ksp

- The Ksp of NiCO3 is 1.4 x 10-7 at 25°C. Calculate its molar solubility.

$$NiCO_{3\,(s)} \leftrightarrows Ni^{2+}{}_{(aq)} + CO_3{}^{2-}{}_{(aq)}$$

----	----
+ s	+ s
s	s

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

$1.4 \times 10^{-7} = s^2$

$s = \sqrt{1.4 \times 10^{-7}}$ = **3.7×10^{-4} M**

Other ways to express solubility...

- We just saw that the solubility of nickel (II) carbonate is 3.7 x 10^{-4} mol/L. What mass of $NiCO_3$ is needed to prepare 500 mL of saturated solution?

$$\frac{3.7 \times 10^{-4}\,\text{mol}\,NiCO_3}{1\,\text{L}} \times \frac{0.500\,\text{L}}{} \times \frac{118.72\,\text{g}}{1\,\text{mol}\,NiCO_3} = 0.022\,\text{g}$$

0.022 g of $NiCO_3$ will dissolve to make 500 mL solution.

Calculate the solubility of MgF_2 in water. What mass will dissolve in 2.0 L of water?

$$MgF_2\,(s) \leftrightarrows Mg^{2+}\,(aq) + 2\,F^-\,(aq)$$

---- -----

+ s + 2s

s 2s

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

$K_{sp} = 7.4 \times 10^{-11} = 4s^3$

s = **2.6×10^{-4} mol/L**

$$\frac{2.6 \times 10^{-4}\,\text{mol MgF}_2}{1\,\text{L}} \times \frac{2.0\,\text{L}}{} \times \frac{62.31\,\text{g}}{1\,\text{mol MgF}_2} = 0.032\,\text{g MgF}_2$$

Solubility and pH

- Calculate the pH of a saturated solution of silver hydroxide, AgOH. Refer to the table in your booklet for the Ksp of AgOH.

$$AgOH_{(s)} \leftrightarrows Ag^+_{(aq)} + OH^-_{(aq)}$$

	----	----
	+ s	+ s
	s	s

Ksp = $2.0 \times 10^{-8} = [Ag^+][OH^-] = s^2$

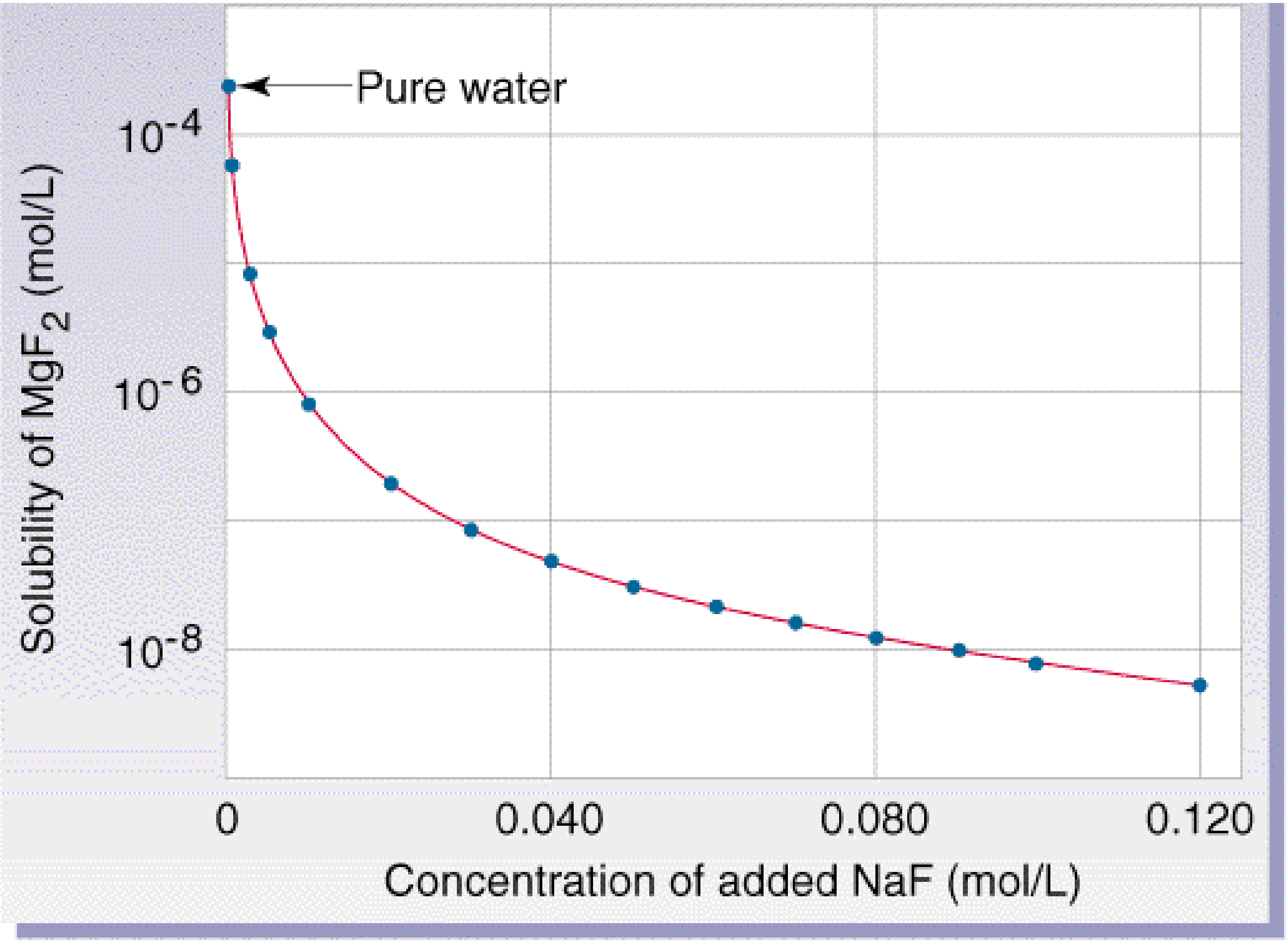
$s = 1.4 \times 10^{-4}$ M = $[OH^-]$

pOH = $-\log(1.4 \times 10^{-4}) = 3.85$

pH = 14.00 - pOH = **10.15**

The **Common Ion Effect** on Solubility

The solubility of MgF_2 in pure water is 2.6×10^{-4} mol/L. What happens to the solubility if we dissolve the MgF_2 in a solution of NaF, instead of pure water?



Calculate the solubility of MgF_2 in a solution of 0.080 M NaF.

MgF_2 (s) ⇆ Mg^{2+} (aq) + 2 F^- (aq)

---- ~~0.080 M~~

+ s + 2s

s 0.080 + 2s

$K_{sp} = 7.4 \times 10^{-11} = [Mg^{2+}][F^-]^2 = (s)(0.080 + 2s)^2$

Since Ksp is so small…assume that 2s << 0.080

$7.4 \times 10^{-11} = (s)(0.080)^2$

s = **1.2 x 10^{-8} mol/L**

Explaining the Common Ion Effect

The presence of a common ion in a solution will lower the solubility of a salt.

- LeChatelier's Principle:

The addition of the common ion will shift the solubility equilibrium backwards. This means that there is more solid salt in the solution and therefore the solubility is lower!

Ksp and Solubility

- Generally, it is fair to say that salts with very small solubility product constants (Ksp) are only sparingly soluble in water.
- When comparing the solubilities of two salts, however, you can sometimes simply compare the relative sizes of their Ksp values.
- This works if the salts have the same number of ions!
- For example… CuI has Ksp = 5.0×10^{-12} and $CaSO_4$ has Ksp = 6.1×10^{-5}. Since the Ksp for calcium sulfate is larger than that for the copper (I) iodide, we can say that calcium sulfate is more soluble.

But be careful...

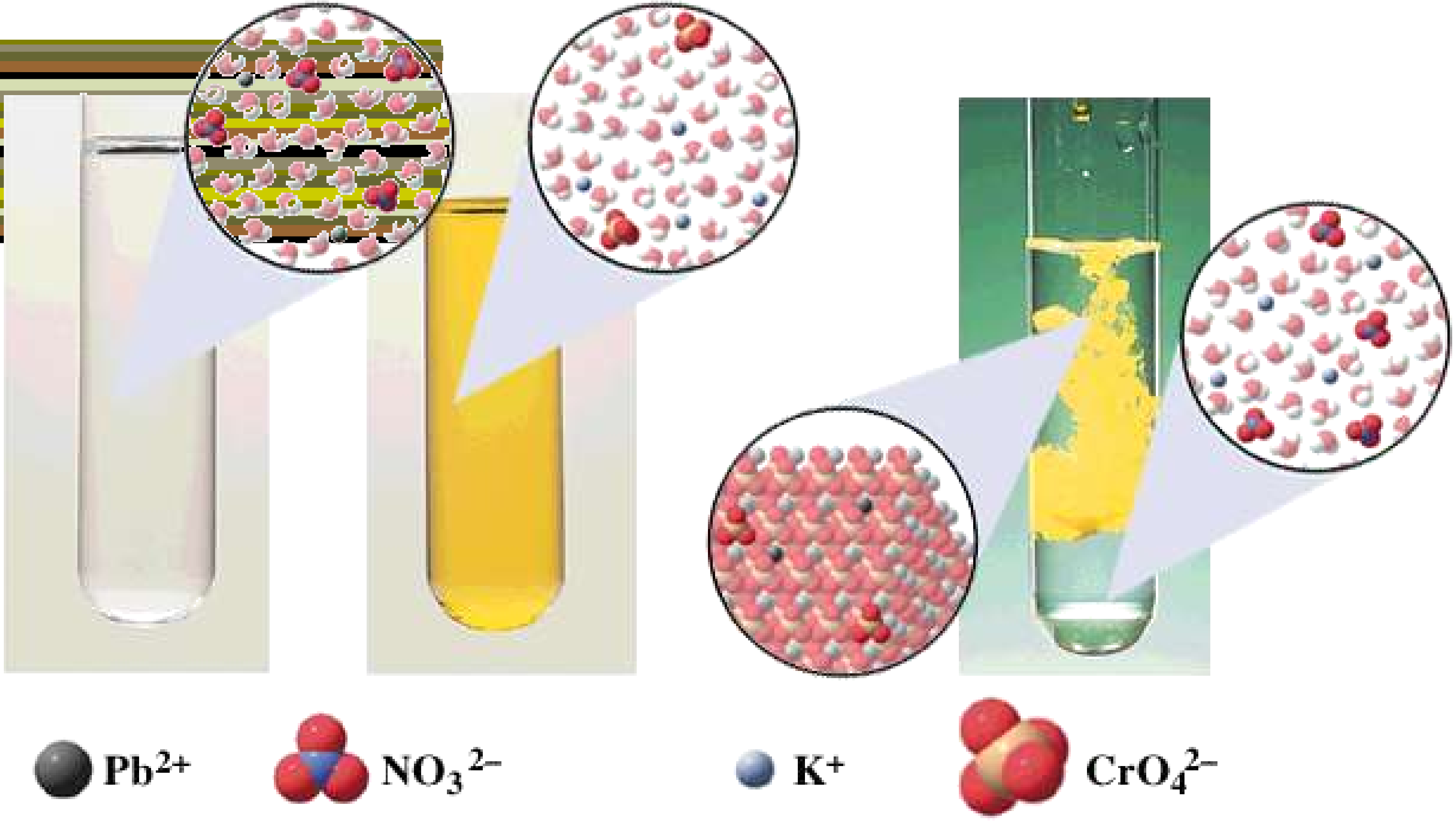
Salt	Ksp	Solubility (mol/L)
CuS	8.5×10^{-45}	9.2×10^{-23}
Ag_2S	1.6×10^{-49}	3.4×10^{-17}
Bi_2S_3	1.1×10^{-73}	1.0×10^{-15}

Do you see the “problem” here??

Mixing Solutions - Will a Precipitate Form?

If 15 mL of 0.024-M lead nitrate is mixed with 30 mL of 0.030-M potassium chromate - will a precipitate form?

$$Pb(NO_3)_2\ (aq) + K_2CrO_4\ (aq) \leftrightarrows PbCrO_4\ (s) + 2\ KNO_3\ (aq)$$



$$Pb(NO_3)_2\ (aq) + K_2CrO_4\ (aq) \leftrightarrows PbCrO_4\ (s) + 2\ KNO_3\ (aq)$$

Step 1: Is a sparingly soluble salt formed?

We can see that a double replacement reaction can occur and produce $PbCrO_4$. Since this salt has a very small Ksp, it may precipitate from the mixture. The solubility equilibrium is:

$$PbCrO_4\ (s) \leftrightarrows Pb^{2+}\ (aq) + CrO_4^{2-}\ (aq)$$

$$Ksp = 2 \times 10^{-16} = [Pb^{2+}][CrO_4^{2-}]$$

If a precipitate forms, it means the solubility equilibrium has shifted BACKWARDS.

This will happen only if Qsp > Ksp in our mixture.

Step 2: Find the concentrations of the ions that form the sparingly soluble salt.

Since we are mixing two solutions in this example, the concentrations of the Pb^{2+} and CrO_4^{2-} will be diluted. We have to do a <u>dilution calculation</u>!

Dilution: $C_1V_1 = C_2V_2$

$$[Pb^{2+}] = \frac{C_1V_1}{V_2} = \frac{(0.024\,\text{M})(15\,\text{mL})}{(45\,\text{mL})} = 0.0080\,\text{M}\ \ Pb^{2+}$$

$$[CrO_4^{2-}] = \frac{C_1V_1}{V_2} = \frac{(0.030\,\text{M})(20\,\text{mL})}{(45\,\text{mL})} = 0.020\,\text{M}\ \ CrO_4^{2-}$$

Step 3: Calculate Qsp for the mixture.

$Qsp = [Pb^{2+}][CrO_4^{2-}] = (0.0080\ M)(0.020\ M)$

$Qsp = 1.6 \times 10^{-4}$

Step 4: Compare Qsp to Ksp.

Since Qsp >> Ksp, a precipitate will form when the two solutions are mixed!

Note: If Qsp = Ksp, the mixture is saturated

If Qsp < Ksp, the solution is unsaturated

Either way, no ppte will form!