SLIGHTLY SOLUBLE SOLIDS

- When a slightly soluble ionic compound is mixed with water, one of the following two phenomena may occur:

1. The amount of ionic compound is very small. As such:

   - it completely dissolves (completely dissociates into ions)
   - an unsaturated solution is formed
   - no undissolved solid remains

$$CaCO_3\ (s) \xrightarrow{H_2O} Ca^{2+}\ (aq) + CO_3^{2-}\ (aq)$$

2. The amount of ionic compound is relatively large. As such:

   - it partially dissolves in water (partially dissociates into ions)
   - a saturated solution is formed
   - some of the solid remains undissolved
   - an equilibrium occurs between the undissolved solid and the ions in the solution

$$CaCO_3\ (s) \overset{H_2O}{\rightleftharpoons} Ca^{2+}(aq) + CO_3^{2-}(aq)$$

Solubility Equilibrium

- The equilibrium constant for the solubility process is called the Solubility Product Constant of $CaCO_3$ (K_{sp})

$$\mathbf{K_{sp} = [Ca^{2+}]\ [CO_3^{2-}]}$$

THE SOLUBILITY PRODUCT CONSTANT (K_{sp})

- K_{sp} is the equilibrium constant for the solubility equilibrium of a slightly soluble (or nearly insoluble) ionic compound.
- K_{sp} equals the product of the equilibrium concentrations of the ions, raised to a power equal to the number of the ions in the formula of the compound
- K_{sp} depends on the concentration of the ions and is temperature dependent (constant at a given temperature)

Examples:

Write the solubility product expressions for the following compounds:

1) $Mg(OH)_2$

$$Mg(OH)_2\ (s) \rightleftharpoons Mg^{2+}\ (aq) + 2\ OH^-\ (aq)$$

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

2) $Ca_3(PO_4)_2$

$$Ca_3(PO_4)_2\ (s) \rightleftharpoons 3\ Ca^{2+}(aq) + 2\ PO_4^{3-}\ (aq)$$

$$K_{sp} = [Ca^{2+}]^3\ [PO_4^{3-}]^2$$

3) Ag_2S

$$Ag_2S\ (s) \rightleftharpoons$$

$K_{sp} =$

CALCULATING K_{SP} FROM SOLUBILITY

1. K_{sp} of a slightly soluble ionic compound is expressed in terms of the molar concentrations of ions in the saturated solution.
2. It is related to the **molar solubility** of the ionic compound
3. **Molar Solubility** = moles of compound that dissolve in 1 L of water to give a saturated solution.

Examples:

1. The solubility of silver chromate, Ag_2CrO_4 , in water is 0.022 g/L. Calculate K_{sp} for Ag_2CrO_4

(a) First calculate the Molar Solubility:

$$? \frac{\text{moles}}{\text{L}} = \frac{0.022 \text{ g } Ag_2CrO_4}{1 \text{ L water}} \times \frac{1 \text{ mole } Ag_2CrO_4}{332 \text{ g } Ag_2CrO_4} = 6.\underline{6}2 \times 10^{-5} \text{ M}$$

(b) Next, consider the Solubility Equilibrium:

	$Ag_2CrO_4\ (s) \rightleftharpoons$	$2\ Ag^{+}\ (aq)$ +	$CrO_4^{2-}\ (aq)$
Initial	-----	0	0
Δ	-----	+2 x	+ x
Equilibrium	-----	+2 x	+ x

(c) Write K_{sp} expression and substitute the molar concentrations of the ions in the saturated solution:

$$K_{sp} = [Ag^+]^2\ [CrO_4^{\ 2-}] = (2x)^2\ (x) = 4\ x^3 \qquad x = 6.\underline{6}2 \times 10^{-5} \text{ M}$$

$$K_{sp} = [2(6.\underline{6}2 \times 10^{-5})]^2\ [6.\underline{6}2 \times 10^{-5}] = 1.2 \times 10^{-12}$$

2. $PbSO_4$ is used as a white pigment and in car batteries. Its solubility is 4.25×10^{-3} g/100 mL solution. What is K_{sp} for $PbSO_4$?

CALCULATING SOLUBILITY FROM K_{SP}

Examples:

1. What is the molar solubility of MgF_2 in water? The K_{sp} for MgF_2 is 7.4×10^{-11}

   Let x = the molar solubility of MgF_2

	MgF_2 (s) ⇌	Mg^{2+} (aq) +	$2\,F^-$ (aq)
Initial	-----	0	0
Δ	-----	+ x	+ 2 x
Equilibrium	-----	+ x	+ 2 x

   Substitute from the table into the equilibrium-constant expression:

   $[Mg^{2+}]\,[F^-]^2 = Ksp$

   $(x)\,(2x)^2 = 4x^3 = 7.4 \times 10^{-11}$ $\qquad x = \sqrt[3]{\dfrac{7.4 \times 10^{-11}}{4}} = 2.6 \times 10^{-4}$ M

2. The Ksp of magnesium carbonate is 1.0×10^{-5}. Calculate the solubility of magnesium carbonate in grams per liter of water.

   Let x = molar solubility of $MgCO_3$

	$MgCO_3$ (s) ⇌	Mg^{2+} (aq) +	CO_3^{2-} (aq)
Initial	-----	0	0
Δ	-----	+ x	+ x
Equilibrium	-----	+ x	+ x

   $[Mg^{2+}]\,[CO_3^{2-}] = Ksp$

   $(x)\,(x) = x^2 = 1.0 \times 10^{-5}$ $\qquad x = \sqrt[3]{(1.0 \times 10^{-5})} = 3.\underline{1}6 \times 10^{-3}$ M

   $$? \frac{\text{g } MgCO_3}{\text{L water}} = \frac{3.\underline{1}6 \times 10^{-3} \text{ moles}}{\text{L water}} \times \frac{84.32 \text{ g}}{1 \text{ mol } MgCO_3} = 0.27 \text{ g/L}$$

SOLUBILITY AND THE COMMON ION EFFECT

- Consider the solubility of one salt in the solution of another salt having the same cation or anion:

Ex:	Solubility of AB in AC	Common cation:	A^+
	Solubility of AB in DB	Common anion:	B^-

- The effect of the common ion is to **decrease the solubility** of the salt

Example:
Consider what happens to the solubility of calcium oxalate, CaC_2O_4 in a solution of calcium chloride, $CaCl_2$

In pure water: $CaC_2O_4\,(s) \rightleftharpoons \mathbf{Ca^{2+}\,(aq)} + C_2O_4^{\;2-}\,(aq)$

Add $CaCl_2$: (soluble salt) $CaCl_2\,(aq) \longrightarrow \mathbf{Ca^{2+}\,(aq)} + 2\,Cl^-\,(aq)$

Result:

- An increase in the concentration of $[Ca^{2+}]$ ions
- This is a "stress" on the solubility equilibrium of $CaC_2O_4(s)$
- The solubility equilibrium will shift to the left
- Some CaC_2O_4 will precipitate from the solution
- The solution will contain less dissolved $C_2O_4^{2-}(aq)$ ions

Conclusion:

- **Ca**$C_2O_4(s)$ is less soluble in a solution of **Ca**Cl_2 than in pure water

Application:

- Kidney stones form when the concentrations of Ca^{2+} ions are sufficiently great and calcium oxalate or phosphate slowly precipitates in the kidney.

SOLUBILITY CALCULATIONS INVOLVING COMMON ION

Examples:

1. The solubility of silver sulfate, in water is 8.0 g/L at 25°C. Calculate the molar solubility of silver sulfate in water and in a 0.65 M solution of sodium sulfate at 25°C ? K_{sp} of silver sulfate is not available.

(a) First calculate molar solubility of Ag_2SO_4 in water

$$? \frac{\text{moles}}{\text{L water}} = \frac{8.0 \text{ g } Ag_2SO_4}{1 \text{ L water}} \times \frac{1 \text{ mole } Ag_2SO_4}{311.81 \text{ g}} = 0.02\underline{5}65 \text{ M}$$

(b) Calculate Ksp of Ag_2SO_4

	Ag_2SO_4 (s) $\rightleftharpoons$	2 Ag^+ (aq) +	SO_4^{2-} (aq)
Initial	-----	0	0
Δ	-----	+ 2 x	+ x
Equilibrium	-----	+ 2 x	+ x

Ksp = $[Ag^{2+}]^2 [SO_4^{2-}] = (2x)^2 (x) = 4x^3$ x = 0.02$\underline{5}$65 M

K_{sp} = $(2 \times 0.02\underline{5}65)^2 (0.02\underline{5}65) = 6.\underline{7}55 \times 10^{-5}$

(c) Use Ksp to calculate the molar solubility of Ag_2SO_4 in 0.65 M Na_2SO_4

	Ag_2SO_4 (s) $\rightleftharpoons$	2 Ag^+ (aq) +	SO_4^{2-} (aq)
Initial	-----	0	0.65
Δ	-----	+ 2 x	+ x
Equilibrium	-----	+ 2 x	0.65 + x

$[Ag^{2+}]^2 [SO_4^{2-}]$ = Ksp $(2x)^2 (0.65 + x)$ = Ksp

Assume that: x <<<<<<< 0.65 It follows: $0.65 + x \approx 0.65$

Then: $(2x)^2 (0.65) = \text{Ksp} = 6.\underline{7}55 \times 10^{-5}$

$2.6\ x^2 = 6.755 \times 10^{-5}$ $x = \sqrt[3]{\dfrac{6.755 \times 10^{-5}}{206}} = 5.097 \times 10^{-3}$ M

Check if assumption was correct:
$0.65 + 0.005097 \approx 0.65$ Yes, it was correct

Compare:

0.02565 M = molar solubility of Ag_2SO_4 in water

0.00051 M = molar solubility of Ag_2SO_4 in 0.65 M Na_2SO_4 (much less)

2. Which of the following compounds should most affect the solubility of $PbSO_4$,lead(II) sulfate, in water to which it has been added ?

(a) Na_2SO_4 (b) PbS (c) NaCl

$$PbSO_4(s) \rightleftharpoons \mathbf{Pb^{2+}(aq)} + \mathbf{SO_4^{2-}(aq)}$$

Na_2SO_4	**PbS**	**NaCl**
soluble salt	practically insoluble salt	soluble salt
K_{sp} not listed	$K_{sp} = 2.5 \times 10^{-27}$	K_{sp} not listed
SO_4^{2-} is common ion	**Pb^{2+}** is common ion	no common ion
decreases the solubility of $PbSO_4$ considerably	decreases the solubility of $PbSO_4$ very little	no effect on the solubility of $PbSO_4$

NOTE: Some basic solubility rules must be memorized at this point

Start by memorizing simple rules:

1. All **Na^+, K^+, and NH_4^+** salts are **soluble** (no exceptions)
2. All nitrates (**NO_3^-**) are **soluble** (no exceptions)
3. All sulfides (**S^{2-}**) are **insoluble** (exceptions: Na^+, K^+, and NH_4^+ salts)

PRECIPITATION CALCULATIONS

- What concentration of ions will cause a substance:

  TO PRECIPITATE OR REMAIN IN SOLUTION ?

- The answer is provided by the evaluation of Qc (reaction quotient)

Recall :

- **If Qc < Keq** Reaction goes in the forward direction $\longrightarrow$
- **If Qc > Keq** Reaction goes in the reverse direction $\longleftarrow$
- **If Qc = Keq** Reaction mixture is at equilibrium $\rightleftharpoons$

For a solubility equilibrium:

$$AB\,(s) \underset{\text{precipitation}}{\overset{\text{dissolution}}{\rightleftarrows}} A^{+}\,(aq) + B^{-}\,(aq)$$

$Qc = [A^{+}]\,[B^{-}]$ = Ion Product

$Q_c < K_{sp}$	$Q_c = K_{sp}$	$Q_c > K_{sp}$
Solution is unsaturated	Solution is saturated	Solution is saturated
Ionic compounds remain dissolved in solution	Ionic compound remains dissolved in solution Reaction is at equilibrium	Ionic compound precipitates

Examples:

1. Assume a solution containing: 0.050 M Pb^{2+} and 0.10 M Cl^{-}
   Will $PbCl_2$ precipitate? (Ksp = 1.6×10^{-5})

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,Cl^{-}(aq)$$

$Qc = [Pb^{2+}]_i\,[Cl^{-}]_i^2$

where: $[Pb^{2+}]_i$ = initial concentration of Pb^{2+} = 0.050 M
$[Cl^{-}]_i$ = initial concentration of Cl^{-} = 0.10 M

Qc $= [Pb^{2+}]_i\,[Cl^{-}]_i^2 = [0.050\text{ M}]\,[0.10]^2 =$ **5.0×10^{-4}**

NOTE: $5.0 \times 10^{-4} > 1.6 \times 10^{-5}$

Qc > Ksp **Precipitation will occur**

$$PbCl_2(s) \longleftarrow Pb^{2+}(aq) + 2\,Cl^{-}(aq)$$

Result:

- Because of precipitation, the ion concentrations decrease (Qc decreases)
- Precipitation ceases when Qc = Ksp

2. One form of kidney stones is calcium phosphate, $Ca_3(PO_4)_2$, which has a Ksp of 1×10^{-26}. A sample of urine contains 1.0×10^{-3} M Ca^{2+} and 1.0×10^{-8} M PO_4^{3-}. Calculate Qc and predict whether $Ca_3(PO_4)_2$ will precipitate.

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3\,Ca^{2+}(aq) + 2\,PO_4^{3-}(aq)$$

$Qc = [Ca^{2+}]_i^3\,[PO_4^{3-}]_i^2$

where: $[Ca^{2+}]_i$ = initial concentration of Ca^{2+} = 1.0×10^{-3} M
$[PO_4^{3-}]_i$ = initial concentration of PO_4^{3-} = 1.0×10^{-8} M

Qc $= \mathbf{(1.0 \times 10^{-3})^3\,(1.0 \times 10^{-8})^2 =}$ **1.0×10^{-25}**

NOTE: $1.0 \times 10^{-25} > 1.0 \times 10^{-26}$

Qc > Ksp **Precipitation will occur**

$$Ca_3(PO_4)_2(s) \longleftarrow 3\,Ca^{2+}(aq) + 2\,PO_4^{3-}(aq)$$

3. Exactly 0.400 L of 0.50 M Pb^{2+} and 1.60 L of 2.50 x 10^{-2} M Cl^{-} are mixed together. Calculate Qc and predict whether $PbCl_2$ will precipitate. The Ksp of $PbCl_2$ is 1.6 x 10^{-5}.

First: **Calculate the molar concentrations of each ion present**

(Assume that the total volume of the solution after mixing equals the sum of the volumes of the separate solutions)

Total Volume = 0.400 L + 1.60 l = 2.00 L

$$[Pb^{2+}] = 0.50 \text{ M} \times \frac{0.400 \text{ L}}{2.00 \text{ L}} = 0.10 \text{ M}$$

$$[Cl^{-}] = 2.50 \text{ M} \times \frac{1.60 \text{ L}}{2.00 \text{ L}} = 0.0200 \text{ M}$$

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,Cl^{-}(aq)$$

$$Qc = [Pb^{2+}]_i [Cl^{-}]_i^2 = [0.10 \text{ M}]\,[0.0200]^2 = 4.0 \times 10^{-5}$$

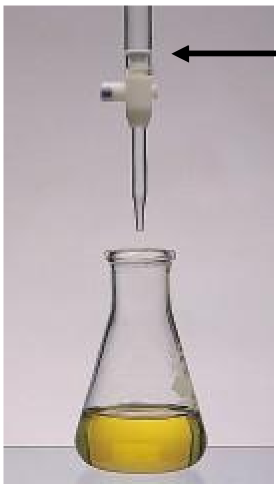
NOTE: $4.0 \times 10^{-5} > 1.6 \times 10^{-5}$

Qc > Ksp **Precipitation will occur**

4. The phosphate in natural waters often precipitates as insoluble salts such as $Ca_3(PO_4)_2$. In a certain river, $[Ca^{2+}] = [PO_4^{3-}] = 1.0 \times 10^{-9}$ M. Will $Ca_3(PO_4)_2$ precipitate? If not, what must the concentration of phosphate ions be for precipitation to occur? K_{sp} of $Ca_3(PO_4)_2 = 1.2 \times 10^{-29}$

FRACTIONAL PRECIPITATION

- The technique of separating two or more ions from a solution by adding a reactant that precipitates first one ion, then another, is called **fractional precipitation**.
- For example, suppose a solution contains **0.10 M Ba^{2+}** and **0.10 M Sr^{2+}**.
  - The two ions can be separated by slowly adding a concentrated solution of **K_2CrO_4**
  - [Ksp ($BaCrO_4$) = 1.2×10^{-10}] and [Ksp ($SrCrO_4$) = 3.5×10^{-5}]
  - **$BaCrO_4$** will precipitate **first**; **$SrCrO_4$** will precipitate second. Why?



K_2CrO_4

0.10 M **Ba^{2+}**
\+
0.10 M **Sr^{2+}**
\+
small amt. of **K_2CrO_4**

- What is the concentration of K_2CrO_4 necessary to just begin the precipitation of **$BaCrO_4$**?

  $[Ba^{2+}][CrO_4^{2-}]$ = Ksp (for $BaCrO_4$) = 1.2×10^{-10}

  $[0.10\ M][CrO_4^{2-}] = 1.2 \times 10^{-10}$ **$[CrO_4^{2-}] = 1.2 \times 10^{-9}$ M**

- What is the concentration of K_2CrO_4 necessary to just begin the precipitation of **$SrCrO_4$**?

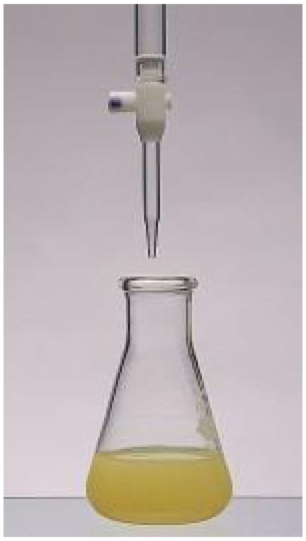
  $[Sr^{2+}][CrO_4^{2-}]$ = Ksp (for $SrCrO_4$) = 3.5×10^{-5}

  $[0.10\ M][CrO_4^{2-}] = 3.5 \times 10^{-5}$ $[CrO_4^{2-}] = 3.5 \times 10^{-4}$ **M**

Note: **$[CrO_4^{2-}]$ to ppt Ba^{2+} < $[CrO_4^{2-}]$ to ppt Sr^{2+}**

1.2×10^{-9} M < 3.5×10^{-4} M

Precipitation and separation of $BaCrO_4$



1. K_2CrO_4 is slowly being added from the buret.
2. When the concentration of $[CrO_4^{2-}]$ reaches 1.2×10^{-9} M Ba^{2+} will start to precipitate as $BaCrO_4$
3. More Ba^{2+} will continue to precipitate as more K_2CrO_4 is being added.
4. No Sr^{2+} will precipitate as long the $[CrO_4^{2-}] < 3.5 \times 10^{-4}$
5. The addition of K_2CrO_4 can be stopped just before $[CrO_4^{2-}]=3.5 \times 10^{-4}$ M and the $BaCrO_4$ precipitate can be filtered off.

Is there any dissolved Ba^{2+} left in solution? YES

Is the amount of dissolved Ba^{2+} left in solution significant ?

$[Ba^{2+}]\,[CrO_4^{2-}] = K_{sp}\ (\text{for } BaCrO_4) = 1.2 \times 10^{-10}$

$[Ba^{2+}]\,[3.5 \times 10^{-4}] = 1.2 \times 10^{-10}$ $[Ba^{2+}] = 3.4 \times 10^{-7}$ M

$$\%\ Ba^{2+} \text{ ion remaining} = \frac{3.4 \times 10^{-7}\ \text{M}}{\text{Initial Concentration}} \times 100 = \frac{3.4 \times 10^{-7}\ \text{M}}{0.10\ \text{M}} \times 100 = \mathbf{0.00034\ \%}$$

insignificant

Conclusion:

- Most of the Ba^{2+} ion can be removed by filtration before the Sr^{2+} precipitates.

QUALITATIVE EFFECT OF PH ON SOLUBILITY

- Consider the solubility equilibrium of calcium oxalate, CaC_2O_4 :

$$CaC_2O_4(s) \rightleftharpoons Ca^{2+}(aq) + C_2O_4^{2-}(aq)$$

- What would be effect (if any) of lowering the pH on the solubility equilibrium?
  CaC_2O_4 is the salt of a weak acid (oxalic acid, $H_2C_2O_4$)

- Recall: pH is lowered when $[H_3O]^+$ is increased (acid is added)

- $C_2O_4^{2-}$ **is the conjugate base of the weak acid** $HC_2O_4^-$

Therefore:

$$\underset{\text{oxalate ion}}{C_2O_4^{2-}} + H_3O^+ \rightleftharpoons \underset{\text{hydrogen oxalate ion}}{HC_2O_4^-} + H_2O$$

- Equilibrium is shifted to the right (products are favored)

$$CaC_2O_4(s) \rightleftharpoons Ca^{2+}(aq) + C_2O_4^{2-}(aq)$$

H_3O^+ added → $C_2O_4^{2-}$ → **($HC_2O_4^-$ + H_2O) formed**

Result:

1. **$C_2O_4^{2-}(aq)$ is removed** from the solubility equilibrium

2. According to Le Chatelier's principle, the solubility **equilibrium will shift to the right**

3. More $CaC_2O_4(s)$ will dissolve

Conclusion:

- **Salts of weak acids are more soluble in acidic solution (pH < 7) than in pure water (pH = 7**

Example:

Which salt would have its solubility more affected by lowering the pH, AgCl or AgCN?

- AgCl is the salt of **HCl (strong acid)**

$$AgCl\,(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq)$$

H_3O^+ added → No Rxn

- Cl^- is not removed from the solubility equilibrium
- Solubility equilibrium will not shift
- **The solubility of AgCl is unaffected**

- AgCN is the salt of **HCN (weak acid)**

$$AgCN(s) \rightleftharpoons Ag^{+}(aq) + CN^{-}(aq)$$

H_3O^+ added → $HCN + H_2O$

- CN^- is removed from the solubility equilibrium
- Solubility equilibrium will shift to the right
- **The solubility of AgCN increases**

Generalization:

- Lowering of the pH (increased acidity) increases the solubility of salts derived from weak acids but has no effect on the solubility of salts derived from strong acids.

SEPARATION OF METAL IONS BY SULFIDE PRECIPITATION

Solubility Rule:

- **All sulfides (S^{2-}) are insoluble in water** except Na_2S, K_2S and $(NH_4)_2S$

- **Do sulfides, which are insoluble in water dissolve in acidic solution?**

  Note: Sulfides are the salts of hydrosulfuric acid, $H_2S(aq)$, a weak acid.

- Consider a solution containing Zn^{2+} and Pb^{2+} to which $H_2S(aq)$ is added:

$$Zn^{2+}(aq) + S^{2-}(aq) \rightleftharpoons ZnS(s) \qquad Ksp = 1.1 \times 10^{-21} \text{ (more soluble)}$$

$$Pb^{2+}(aq) + S^{2-}(aq) \rightleftharpoons PbS(s) \qquad Ksp = 2.5 \times 10^{-27} \text{ (less soluble)}$$

- Whether ZnS and/or PbS precipitates depends greatly on the **$[S^{2-}]$** ion concentration

- **The higher the $[S^{2-}]$, the more likely that the salt will precipitate**.

- The concentration of **$[S^{2-}]$** can be controlled by adjusting the pH: $H_2S(aq)$ is a weak diprotic acid which ionizes partially in 2 steps:

$$H_2S(aq) + H_2O \rightleftharpoons H_3O^+(aq) + HS^-(aq)$$

$$HS^-(aq) + H_2O \rightleftharpoons H_3O^+(aq) + S^{2-}(aq)$$

- **Lowering of the pH (addition of H_3O^+)**
  - will shift both ionization equilibria to the left
  - **will decrease the concentration of $[HS^-]$ and consequently the conc. of $[S^{2-}]$ ions**
  - permits the precipitation of the least soluble sulfide (PbS) while maintaining the Zn^{2+} in solution. PbS(s) can be filtered off and separated from dissolved $Zn^{2+}(aq)$ ions.