Solubility Equilibria
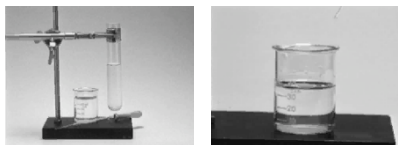*(Qualitative Analysis)*

Solubility Equilibria in Aqueous Systems

K_{sp} (Equilibria of Slightly Soluble Salts, Ionic Compounds)

Factors that Affect Solubility
(Common Ion Effect, Acid-Base Chemistry)

Applications of Ionic Equilibria to Chemical Analysis

Saturated vs. Unsaturated
Solutions of Slightly Soluble AgCl

Equilibria of Slightly Soluble Ionic Compounds

When a solution becomes saturated and a precipitate forms, a cloudiness appears, which is the insoluble solute. Small amounts of ionized solute remain in solution. A representation of the equilibrium relative to the concentrations of the ions is referred to as the:
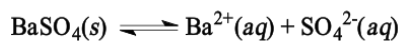*"Solubility Product"*
or the *"Solubility-Product Constant"* :
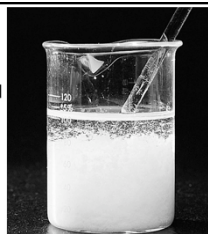$$K_{sp}$$

Solubility-Product Constant, K_{sp}

- Consider

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

$$K_{sp} = [Ba^{2+}][SO_4^{2-}]$$

- ($BaSO_{4(s)}$ is ignored because it is a pure solid so its concentration is constant, i.e., a heterogeneous equilibrium)

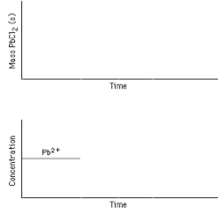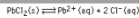$PbCl_2$, a Slightly Soluble Ionic Compound

- *Is there really any Lead ion in solution?*
- *How can this question be answered?*

$PbCl_{2(S)}$ Equilibrium

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

Writing Solubility Product Expressions for Slightly Soluble Ionic Compounds

Problem: Write the solubility product expression for :
(a) silver bromide;
(b) strontium phosphate
(c) aluminum carbonate
(d) nickel(III) sulfide.(The sulfide ion acts as a base and dissociates water to produce SH^- and OH^- .)
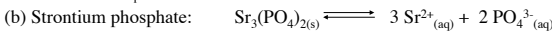
Approach: Write the equation for a saturated solution, then write the expression for the solubility product.

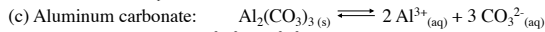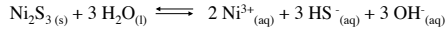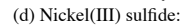### Writing Solubility Product Expressions for Slightly Soluble Ionic Compounds

Solutions:

(a) Silver bromide: $AgBr_{(s)} \rightleftharpoons Ag^+_{(aq)} + Br^-_{(aq)}$

$\qquad K_{sp} = [Ag^+]\,[Br^-]$

(b) Strontium phosphate: $Sr_3(PO_4)_{2(s)} \rightleftharpoons 3\,Sr^{2+}_{(aq)} + 2\,PO_4^{3-}_{(aq)}$

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

(c) Aluminum carbonate: $Al_2(CO_3)_{3\,(s)} \rightleftharpoons 2\,Al^{3+}_{(aq)} + 3\,CO_3^{2-}_{(aq)}$

$\qquad K_{sp} = [Al^{3+}]^2[CO_3^{2-}]^3$

(d) Nickel(III) sulfide:

$Ni_2S_{3\,(s)} + 3\,H_2O_{(l)} \rightleftharpoons 2\,Ni^{3+}_{(aq)} + 3\,HS^-_{(aq)} + 3\,OH^-_{(aq)}$

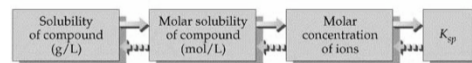$\qquad K_{sp} = [Ni^{3+}]^2[HS^-]^3[OH^-]^3$

K_{sp} of Some Ionic Compounds-Part 1

Solubility-Product Constants (K_{sp}) of Some Ionic Compounds at 25°C

Name, Formula	K_{sp}	Name, Formula	K_{sp}
Carbonates		**Chlorides**	
Barium carbonate, $BaCO_3$	2.0×10^{-9}	Copper (I) chloride, CuCl	1.9×10^{-7}
Cadmium carbonate, $CdCO_3$	1.8×10^{-14}	Lead (II) chloride, $PbCl_2$	1.7×10^{-5}
Calcium carbonate, $CaCO_3$	3.3×10^{-9}	Silver chloride, AgCl	1.8×10^{-10}
Cobalt (II) carbonate, $CoCO_3$	1.0×10^{-10}		
Copper (II) carbonate, $CuCO_3$	3×10^{-12}	**Bromides**	
Lead (II) carbonate, $PbCO_3$	7.4×10^{-14}	Copper (I) bromide, CuBr	5×10^{-9}
Magnesium carbonate, $MgCO_3$	3.5×10^{-8}	Silver bromide, AgBr	5.0×10^{-13}
Mercury (I) carbonate, Hg_2CO_3	8.9×10^{-17}	**Iodides**	
Nickel (II) carbonate, $NiCO_3$	1.3×10^{-7}	Copper (I) iodide, CuI	1×10^{-12}
Strontium carbonate, $SrCO_3$	5.4×10^{-10}	Lead (II) iodide, PbI_2	7.9×10^{-9}
Zinc carbonate, $ZnCO_3$	1.0×10^{-10}	Mercury (I) iodide, Hg_2I_2	4.7×10^{-29}
Chromates		Silver iodide, AgI	8.3×10^{-17}
Barium chromate, $BaCrO_4$	2.1×10^{-10}		
Calcium chromate, $CaCrO_4$	1×10^{-8}		
Lead (II) chromate, $PbCrO_4$	2.3×10^{-13}	**Hydroxides**	
Silver chromate, Ag_2CrO_4	2.6×10^{-12}	Aluminum hydroxide, $Al(OH)_3$	3×10^{-34}
Cyanides		Calcium hydroxide, $Ca(OH)_2$	6.5×10^{-6}
Mercury (I) cyanide, $Hg_2(CN)_2$	5×10^{-40}	Cobalt (II) hydroxide, $Co(OH)_2$	1.3×10^{-15}
Silver cyanide, AgCN	2.2×10^{-16}	Copper (II) hydroxide, $Cu(OH)_2$	2.2×10^{-20}
Halides (Fluorides)		Iron (II) hydroxide, $Fe(OH)_2$	4.1×10^{-15}
Barium fluoride, BaF_2	1.5×10^{-6}	Iron (III) hydroxide, $Fe(OH)_3$	1.6×10^{-39}
Calcium fluoride, CaF_2	3.2×10^{-11}	Magnesium hydroxide, $Mg(OH)_2$	6.3×10^{-10}
Lead (II) fluoride, PbF_2	3.6×10^{-8}	Manganese (II) hydroxide, $Mn(OH)_2$	1.6×10^{-13}
Magnesium fluoride, MgF_2	7.4×10^{-9}	Nickel (II) hydroxide, $Ni(OH)_2$	6×10^{-16}
Strontium fluoride, SrF_2	2.6×10^{-9}	Zinc hydroxide, $Zn(OH)_2$	3×10^{-16}

K_{sp} of Some Ionic Compounds-Part 2

Solubility-Product Constants (K_{sp}) of Some Ionic Compounds at 25°C

| Name, Formula	K_{sp}	Name, Formula	K_{sp}
Iodates		**Sulfates**	
Barium iodate, $Ba(IO_3)_2$	1.5×10^{-9}	Barium sulfate, $BaSO_4$	1.1×10^{-10}
Calcium iodate, $Ca(IO_3)_2$	7.1×10^{-7}	Calcium sulfate, $CaSO_4$	2.4×10^{-5}
Lead (II) iodate, $Pb(IO_3)_2$	2.5×10^{-13}	Lead (II) sulfate, $PbSO_4$	1.6×10^{-8}
Silver iodate, $AgIO_3$	3.1×10^{-8}	Magnesium sulfate, $MgSO_4$	5.9×10^{-3}
Strontium iodate, $Sr(IO_3)_2$	3.3×10^{-7}	Radium sulfate, $RaSO_4$	2×10^{-11}
Zinc iodate, $Zn(IO_3)_2$	3.9×10^{-6}	Silver sulfate, Ag_2SO_4	1.5×10^{-5}
Oxalates		Strontium sulfate, $SrSO_4$	3.2×10^{-7}
Barium oxalate dihydrate, $BaC_2O_4 \cdot 2H_2O$	1.1×10^{-7}	**Sulfides**	
Calcium oxalate monohydrate, $CaC_2O_4 \cdot H_2O$	2.3×10^{-9}	Cadmium sulfide, CdS	1.0×10^{-24}
		Copper (II) sulfide, CuS	8×10^{-34}
		Iron (II) sulfide, FeS	8×10^{-16}
Strontium oxalate monohydrate, $SrC_2O_4 \cdot H_2O$	5.6×10^{-8}	Lead (II) sulfide, PbS	3×10^{-25}
		Manganese (II) sulfide, MnS	3×10^{-11}
Phosphates		Mercury (II) sulfide, HgS	2×10^{-50}
		Nickel (II) sulfide, NiS	3×10^{-16}
Calcium phosphate, $Ca_3(PO_4)_2$	1.2×10^{-29}	Silver sulfide, Ag_2S	8×10^{-48}
Magnesium phosphate, $Mg_3(PO_4)_2$	5.2×10^{-24}	Tin (II) sulfide, SnS	1.3×10^{-23}
Silver phosphate, Ag_3PO_4	2.6×10^{-18}	Zinc sulfide, ZnS	2.0×10^{-22}

Solubility Calculations and Ksp

Determining K_{sp} from Solubility

Problem: Lead chromate is an insoluble compound that at one time was used as the pigment in the yellow stripes on highways. It's solubility is 5.8 x 10^{-6} g/100mL water. What is the K_{sp}?

Approach: *Write the chemical equation for the dissolution of the compound to see the number of ions formed, then write the ion-product expression.*

Determining K_{sp} from Solubility

$$PbCrO_{4\,(s)} \rightleftharpoons Pb^{2+}_{(aq)} + CrO_4^{2-}_{(aq)}$$
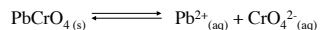
Molar solubility of $PbCrO_4$ = $\dfrac{5.8 \times 10^{-6} g}{100\,mL}$ x $\dfrac{1000\,ml}{1\,L}$ x $\dfrac{1\,mol\ PbCrO_4}{323.2\,g}$

$$= 1.79 \times 10^{-7}\ M\ PbCrO_4$$

1 Mole $PbCrO_4$ = 1 mole Pb^{2+} and 1 mole CrO_4^{2-}

Therefore $[Pb^{2+}] = [CrO_4^{2-}] = 1.79 \times 10^{-7}\ M$

$K_{sp} = [Pb^{2+}]\,[CrO_4^{2-}] = (1.79 \times 10^{-7}\ M)^2 = \mathbf{3.20 \times 10^{-14}}$

Note that the calculated value is different from the table's (**2.3 x 10^{-13}**); is the difference significant? What factors might relate to the difference?

QUESTION #K.1

Calcium phosphate ($Ca_3(PO_4)_2$ is only slightly soluble. In fact, it is common ingredient in phosphate rock and is a major source of phosphate fertilizer. If the molar solubility is 2×10^{-7}, what is the value of the K_{sp}?

A. 3×10^{-34}
B. 2×10^{-10}
C. 3×10^{-32}
D. None of the above.

Determining Solubility from K_{sp}

Problem: Lead chromate used to be used as the pigment for the yellow lines on roads, and is a very insoluble compound. Calculate the solubility of $PbCrO_4$ in water if the K_{sp} is equal to 2.3 x 10^{-13}.

Approach: *Write the chemical equation for the dissolution of the compound to see the number of ions formed, then write the ion-product expression. Solve for [Pb^{2+}] which equals the concentration of $PbCrO_4$ present in solution.*

Determining Solubility from K_{sp}

$$PbCrO_{4\,(s)} \rightleftharpoons Pb^{2+}_{(aq)} + CrO_4^{2-}_{(aq)}$$
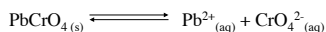
$$K_{sp} = 2.3\ 10^{-13} = [Pb^{2+}]\,[CrO_4^{2-}]$$

Concentration (*M*)	$PbCrO_4$	Pb^{2+}	CrO_4^{2-}
Initial	----------	0	0
Change	----------	+x	+x
Equilibrium	----------	x	x

$$K_{sp} = [Pb^{2+}]\,[CrO_4^{2-}] = (x)(x) = 2.3\ x\ 10^{-13}$$
$$x = 4.80\ x\ 10^{-7}$$

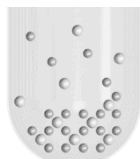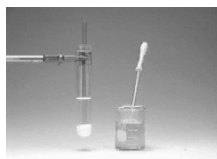Therefore the solubility of $PbCrO_4$ in water is **4.8 x 10^{-7} *M***

QUESTION #K.2

Lead (II) iodide is used in some camera batteries. PbI_2 has a K_{sp} of 1.4×10^{-8}. What is the molar solubility of this compound?

A. 1.9×10^{-3} M
B. 2.4×10^{-3} M
C. 1.5×10^{-3} M
D. 8.4×10^{-5} M

Relative Solubilities
PbCl$_2$ vs. PbCrO$_4$

PbCrO$_4$ solubility in water is **4.8 x 10^{-7} M**
Is PbCl$_2$ >, <, or = to it?
What information do you need to find? **Ksp from table & approximate solubility**

Question: Relative Solubilities
Is PbCl$_2$ more soluble, less soluble or equal to the solubility of PbCrO$_4$?

PbCrO$_4$ solubility in water is **4.8 x 10^{-7} M**

Is PbCl$_2$ >, <, or = to it?
**PbCl$_2$ has a K$_{sp}$ of 1.6 × 10^{-5}**

A) >
B) <
C) =
D) ?

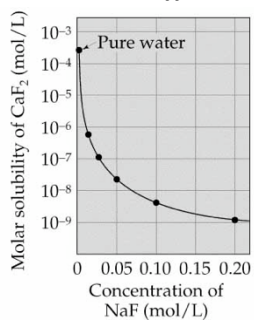## Factors That Affect Solubility:
The Common Ion Effect

- The solubility of a partially soluble salt is decreased when a common ion is added.
- Consider the equilibrium established when acetic acid, HC$_2$H$_3$O$_2$, is added to water.
- At equilibrium H$^+$ and C$_2$H$_3$O$_2^-$ are constantly moving into and out of solution, but the concentrations of ions is constant and equal.
- If a common ion is added, e.g. C$_2$H$_3$O$_2^-$ from NaC$_2$H$_3$O$_2$ (which is a strong electrolyte) then [C$_2$H$_3$O$_2^-$] increases and the system is no longer at equilibrium.
- So, [H$^+$] must decrease.

Visualizing the Common Ion Effect

PbCrO$_{4(s)}$ ⇌ Pb$^{2+}_{(aq)}$ + CrO$_4^{2-}_{(aq)}$ PbCrO$_{4(s)}$ ⇌ Pb$^{2+}_{(aq)}$ + CrO$_4^{2-}_{(aq;\ added)}$
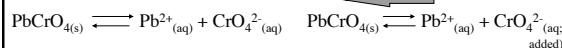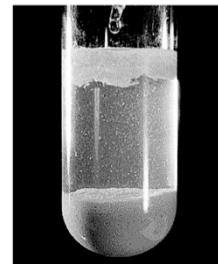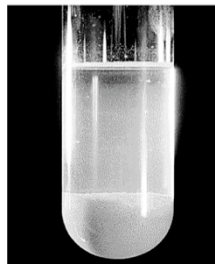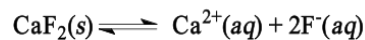
Common-Ion Effect

Common-Ion Effect

- Solubility is decreased when a common ion is added. Therefore the equilibrium shifts to the left.
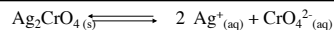- This is an application of Le Châtelier's principle, for eg.:

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$$

- as F$^-$ (from NaF, say) is added, the equilibrium shifts away from the increase.
- Therefore, CaF$_2$(s) is formed and precipitation occurs.
- As NaF is added to the system, the solubility of CaF$_2$ decreases and more precipitate forms.
- *What will happen if a large excess of NaF is added?*

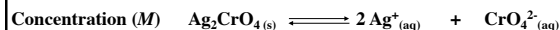## Calculating the Effect of adding a Common Ion on Solubility

Problem: What is the solubility of silver chromate in 0.0600 M silver nitrate solution? K_{sp} = 2.6 x 10^{-12} .

Plan: Write the chemical equation(s) and the solubility-product expression for Ag_2CrO_4. Qualitatively predict what effect the addition of silver ion will have on the solubility of Ag_2CrO_4.

Calculating the Effect of a Common Ion on Solubility

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

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

Concentration (M)	$Ag_2CrO_{4\,(s)}$ $\rightleftharpoons$	$2\,Ag^+_{\,(aq)}$	+	$CrO_4^{2-}_{\,(aq)}$
Initial	---------	0.0600		0
Change	---------	+2x		+x
Equilibrium	---------	0.0600 + 2x		x

Assuming that K_{sp} is small, $0.0600\ M + 2x = 0.600\ M$

K_{sp} = 2.6 x 10^{-12} = (0.0600)^2(x)   x = 7.22 x 10^{-10} M

Therefore, the solubility of silver chromate is **7.22 x 10^{-10} M**

QUESTION #K.3

The K_{sp} of Ag_2CrO_4 is 9.0 × 10^{-12}. What would be the solubility of this compound in a solution that was already 0.10 M in potassium chromate?

A. 9.0 × 10^{-13} M
B. 9.5 × 10^{-6} M
C. 3.0 × 10^{-6} M
D. 4.7 × 10^{-6} M

Effect of pH on Solubility
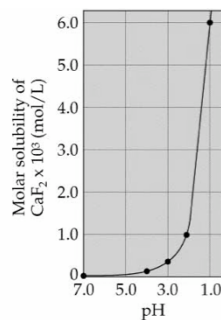
Factors That Affect Solubility:
Acidity / pH

- Again, Le Châtelier's principle applies, for eg.:

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$$

 ❖ If the F$^-$ is removed, then the equilibrium shifts towards the decrease (the right) and CaF_2 dissolves.
 ❖ F$^-$, a weak base,can be removed by adding a strong acid:

$$F^-(aq) + H^+(aq) \rightleftharpoons HF(aq)$$

 ❖ As pH decreases, [H$^+$] increases and solubility increases since fluoride ion is removed as HF.
- The effect of pH on solubility is dramatic.


Solubility and pH

Dissolution of
Mg(OH)$_2$ by Acid

QUESTION

Predict what will happen when the pH of a saturated $Mg(OH)_2$ solution is increased to 12.00. For a saturated $Mg(OH)_2$ solution, the pH = 11.03.

(A) More $Mg(OH)_2$ will dissolve.

(B) Some $Mg(OH)_2$ will precipitate out.

(C) A pH change has no effect on the solubility of $Mg(OH)_2$.

(D) There is insufficient information to make a prediction.

Testing for the Presence of a Carbonate
Solubility, pH and Carbonic Acid
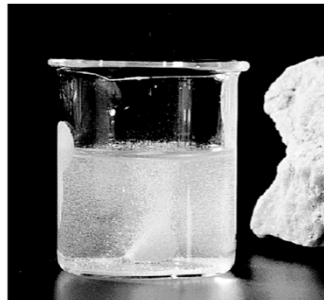
Predicting the Effect on Solubility of Adding Strong Acid

Problem: Write balanced equations to explain whether addition of H_3O^+ from a strong acid affects the solubility of:
(a) Iron (II) cyanide
(b) Potassium bromide
(c) Aluminum hydroxide

Plan: Write the balanced dissolution equation and note the anion. *Anions of weak acids react with H_3O^+ and shift the equilibrium position toward more dissolution. Strong acid anions do not react, so added acid has no effect.*

Predicting the Effect on Solubility of Adding Strong Acid

Solutions:
(a) $Fe(CN)_{2\,(s)} \rightleftharpoons Fe^{2+}_{(aq)} + 2\,CN^-_{(a)}$ **Increases solubility:** CN^- ion is a weak base. It reacts with water to form the weak acid HCN, so it would be removed from the solubility expression.

(b) $KBr_{(s)} \rightleftharpoons K^+_{(aq)} + Br^-_{(aq)}$ **No effect:** Br^- is the anion of a strong acid, and K^+ is the cation of a strong base.

(c) $Al(OH)_{3\,(s)} \rightleftharpoons Al^{3+}_{(aq)} + 3\,OH^-_{(aq)}$ **Increases solubility:** OH^- reacts with the added acid to produce water in a simple acid-base reaction.
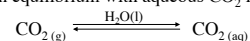

QUESTION #K.4

The solubility of AgCl in water is _____ the solubility of AgCl in strong acid at the same temperature.
A) greater than
B) less than
C) about the same as
D) cannot be determined

The Chemistry of Limestone Formation

Gaseous CO_2 is in equilibrium with aqueous CO_2 in natural waters:

$$CO_{2\,(g)} \underset{H_2O(l)}{\rightleftharpoons} CO_{2\,(aq)}$$

The concentration of CO_2 is proportional to the partial pressure of $CO_{2\,(g)}$ in contact with the water (Henry's Law; section 13.3):

$$[CO_{2\,(aq)}] \text{ (proportional to) } P_{CO_2}$$
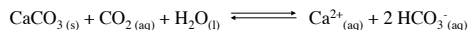

Henry's Law

The Chemistry of Limestone Formation

Gaseous $CO_2 \rightleftharpoons$ aqueous CO_2 continued:

The reaction of CO_2 with water produces H_3O^+:

$$CO_{2\,(aq)} + 2\,H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HCO_3^-{}_{(aq)}$$

Thus, the presence of $CO_{2\,(aq)}$ forms H_3O^+, which increases the solubility of $CaCO_3$:

$$CaCO_{3\,(s)} + CO_{2\,(aq)} + H_2O_{(l)} \rightleftharpoons Ca^{2+}{}_{(aq)} + 2\,HCO_3^-{}_{(aq)}$$

In what complex carbon based system is this a significant factor?

Predicting the Formation of a Precipitate: Q_{sp} vs. K_{sp}

The solubility product constant, K_{sp}, can be compared to Q_{sp} to understand the characteristics of a solution with respect to forming a precipitate.

- $Q_{sp} = K_{sp}$: When a solution becomes saturated, no more solute will dissolve, and the solution is called "saturated." There will be no changes that will occur.

- $Q_{sp} > K_{sp}$: Precipitates will form until the solution becomes saturated.

- $Q_{sp} < K_{sp}$: Solution is unsaturated, and no precipitate will form.

Predicting the Formation of a Precipitate

Problem: Will a precipitate form when 0.100 L of a solution containing 0.55 M barium nitrate is added to 200.00 mL of a 0.100 M solution of sodium chromate?

Plan: We first see if the solutions will yield soluble ions, then we calculate the concentrations, adding the two volumes together to get the total volume of the solution, then we calculate the product constant (Q_{sp}), and compare it to the solubility product constant to see if a precipitate will form.

Predicting the Formation of a Precipitate

Solution: Both Na_2CrO_4 and $Ba(NO_3)_2$ are soluble, so we will have Na^+, CrO_4^{2-}, Ba^{2+} and NO_3^- ions present in 0.300 L of solution. We change partners, look up solubilities, and we find that $BaCrO_4$ would be insoluble, so we calculate it's ion-product constant and compare it to the solubility product constant of 2.1×10^{-10} .

For Ba^{2+}: [0.100 L $Ba(NO_3)_2$] [0.55 M] = 0.055mol Ba^{2+}

$$[Ba^{2+}] = \frac{0.055\ \text{mol Ba}^{2+}}{0.300\ \text{L}} = 0.183\ M\ \text{in Ba}^{2+}$$

Predicting the Formation of a Precipitate

Solution continued

For CrO_4^{2-} : [0.100 M Na_2CrO_4] [0.200 L] = 0.0200 mol CrO_4^{2-}

$$[CrO_4^{2-}] = \frac{0.0200\ \text{mol CrO}_4^{2-}}{0.300\ \text{liters}} = 0.667\ M\ \text{in CrO}_4^{2-}$$

$Q_{sp} = [Ba^{2+}]\,[CrO_4^{2-}] = (0.183\ M\ \text{Ba}^{2+})(0.667\ M\ \text{CrO}_4^{2-}) = 0.121$

Since $K_{sp} = 2.1 \times 10^{-10}$ and $Q_{sp} = 0.121$, **$Q_{sp} \gg K_{sp}$ and a precipitate will form.**

QUESTION #K.4

Will a precipitate of $BaSO_4$ form when 10.0 mL of 0.0010 M barium nitrate are mixed with 20.0 mL of 0.000020 M of sodium sulfate? The K_{sp} of barium sulfate is 1.5×10^{-9}. Prove your answer by reporting the calculated value of Q.

A. Yes; $Q = 2.0 \times 10^{-8}$
B. Yes; $Q = 4.4 \times 10^{-9}$
C. No; $Q = 7.0 \times 10^{-10}$
D. No; $Q = 3.0 \times 10^{-17}$

Formation of Complex Ions

Formation of Complex Ions

- Consider the formation of $Ag(NH_3)_2^+$:

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2(aq)$$

- The $Ag(NH_3)_2^+$ is called a complex ion.
- NH_3 (the attached Lewis base) is called a ligand.
- The equilibrium constant for the reaction is called the formation constant, K_f:

$$K_f = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2}.$$

- Lewis acid-base chemistry affects solubility.

Formation of Complex Ions

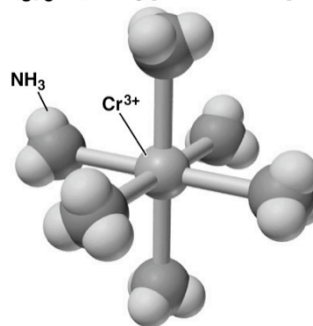- Consider the addition of ammonia to AgCl (white precipitate):

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

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2(aq)$$

- The overall reaction is

$$AgCl(s) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2(aq) + Cl^-(aq)$$
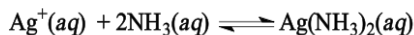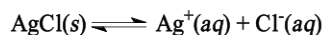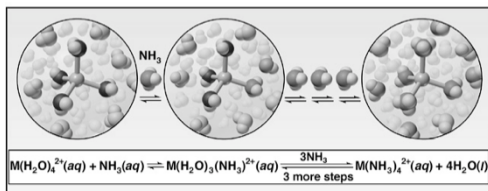
- Effectively, the $Ag^+(aq)$ has been removed from solution.
- By Le Châtelier's principle, the forward reaction (the dissolving of AgCl) is favored.

$Cr(NH_3)_6^{3+}$, a Typical Complex Ion

The Stepwise Exchange of NH_3 for H_2O in $M(H_2O)_4^{2+}$

$$M(H_2O)_4^{2+}(aq) + NH_3(aq) \rightleftharpoons M(H_2O)_3(NH_3)^{2+}(aq) \xrightarrow[\text{3 more steps}]{3NH_3} M(NH_3)_4^{2+}(aq) + 4H_2O(l)$$

Note the values, particularly the order of magnitude (exponent).

Formation Constants for Some Metal Complex Ions in Water at 25°C		
Complex Ion	K_f	**Equilibrium Equation**
$Ag(NH_3)_2^+$	1.7×10^7	$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$
$Ag(CN)_2^-$	1×10^{21}	$Ag^+(aq) + 2CN^-(aq) \rightleftharpoons Ag(CN)_2^-(aq)$
$Ag(S_2O_3)_2^{3-}$	2.9×10^{13}	$Ag^+(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons Ag(S_2O_3)_2^{3-}(aq)$
$CdBr_4^{2-}$	5×10^3	$Cd^{2+}(aq) + 4Br^-(aq) \rightleftharpoons CdBr_4^{2-}(aq)$
$Cr(OH)_4^-$	8×10^{29}	$Cr^{3+}(aq) + 4OH^-(aq) \rightleftharpoons Cr(OH)_4^-(aq)$
$Co(SCN)_4^{2-}$	1×10^3	$Co^{2+}(aq) + 4SCN^-(aq) \rightleftharpoons Co(SCN)_4^{2-}(aq)$
$Cu(NH_3)_4^{2+}$	5×10^{12}	$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons Cu(NH_3)_4^{2+}(aq)$
$Cu(CN)_4^{2-}$	1×10^{25}	$Cu^{2+}(aq) + 4CN^-(aq) \rightleftharpoons Cu(CN)_4^{2-}(aq)$
$Ni(NH_3)_6^{2+}$	1.2×10^9	$Ni^{2+}(aq) + 6NH_3(aq) \rightleftharpoons Ni(NH_3)_6^{2+}(aq)$
$Fe(CN)_6^{4-}$	1×10^{35}	$Fe^{2+}(aq) + 6CN^-(aq) \rightleftharpoons Fe(CN)_6^{4-}(aq)$
$Fe(CN)_6^{3-}$	1×10^{42}	$Fe^{3+}(aq) + 6CN^-(aq) \rightleftharpoons Fe(CN)_6^{3-}(aq)$

Formation Constants (K_f) of Some Complex Ions at 25ºC

Note the values: why are they different from the previous table?

Complex Ion	K_f	
$Ag(CN)_2^-$	3.0×10^{20}	
$Ag(NH_3)_2^+$	1.7×10^7	Are the
$Ag(S_2O_3)_2^{3-}$	4.7×10^{13}	differences from
AlF_6^{3-}	4×10^{19}	the previous table
$Al(OH)_4^-$	3×10^{33}	significant?
$Be(OH)_4^{2-}$	4×10^{18}	
CdI_4^{2-}	1×10^6	
$Co(OH)_4^{2-}$	5×10^9	
$Cr(OH)_4^-$	8.0×10^{29}	
$Cu(NH_3)_4^{2+}$	5.6×10^{11}	
$Fe(CN)_6^{4-}$	3×10^{35}	
$Fe(CN)_6^{3-}$	4.0×10^{43}	

Table Continued

Formation Constants (K_f) of Some Complex Ions at 25ºC

Complex Ion	K_f
$Hg(CN)_4^{2-}$	9.3×10^{38}
$Ni(OH)_4^{2-}$	2×10^{28}
$Pb(OH)_3^-$	8×10^{13}
$Sn(OH)_3^-$	3×10^{25}
$Zn(CN)_4^{2-}$	4.2×10^{19}
$Zn(NH_3)_4^{2+}$	7.8×10^8
$Zn(OH)_4^{2-}$	3×10^{15}

QUESTION

Which of these actions will increase the solubility of $Cu(OH)_2$ in a saturated aqueous solution?

I) A small amount of crystalline $Cu(NO_3)_2$ is added.
II) The solution is buffered at pH = 2.00.
III) Ammonia gas is bubbled through the solution.

A) I and II   **B) II and III**

C) I and III   **D) I, II and III**

Calculating the Concentrations of Complex Ions

Problem: A chemist converts $Ag(H_2O)_2^+$ to the more stable form $Ag(NH_3)_2^+$ by mixing 50.0 L of 0.0020 M $Ag(H_2O)_2^+$ and 25.0 L of 0.15 M NH_3. What is the final $[Ag(H_2O)_2^+]$? $K_f\ Ag(NH_3)_2^+ = 1.7 \times 10^7$.

Plan: Write the equation and the K_f expression, set up the table for the calculation, then substitute into K_f and solve.

Calculating the Concentrations of Complex Ions

Solution:

$$Ag(H_2O)_2^+{}_{(aq)} + 2\ NH_{3\ (aq)} \rightleftharpoons Ag(NH_3)_2^+{}_{(aq)} + 2\ H_2O_{(l)}$$

$$K_f = \frac{[Ag(NH_3)_2^+]}{[Ag(H_2O)_2^+][NH_3]^2} = 1.7 \times 10^7$$

Finding the initial concentrations:

$$[Ag(H_2O)_2^+]_{init} = \frac{50.0\ L \times 0.0020\ M}{50.0\ L + 25.0\ L} = 1.3 \times 10^{-3}\ M$$

$$[NH_3]_{init} = \frac{25.0\ L \times 0.15\ M}{50.0\ L + 25.0\ L} = 5.0 \times 10^{-2}\ M$$

Calculating the Concentrations of Complex Ions

Assume that all of the $Ag(H_2O)_2^+$ is converted $Ag(NH_3)_2^+$; set up the table with x = $[Ag(H_2O)_2^+]$ at equilibrium.
Ammonia reacted = $[NH_3]_{reacted} = 2(1.3 \times 10^{-3}\ M) = 2.6 \times 10^{-3}\ M$

Concentration (M)	$Ag(H_2O)_2^+{}_{(aq)}$	$2NH_{3\ (aq)}$	$\rightarrow Ag(NH_3)_2^+$	$2\ H_2O_{(aq)}$
Initial	1.3×10^{-3}	5.0×10^{-2}	0	----
Change	$\sim(-1.3 \times 10^{-3})$	$\sim(-2.6 \times 10^{-3})$	$\sim(+1.3 \times 10^{-3})$	----
Equilibrium	x	4.7×10^{-2}	1.3×10^{-3}	----

$$K_f = \frac{[Ag(NH_3)_2^+]}{[Ag(H_2O)_2^+][NH_3]^2} = \frac{1.3 \times 10^{-3}}{x(4.7 \times 10^{-2})^2} = 1.7 \times 10^7$$
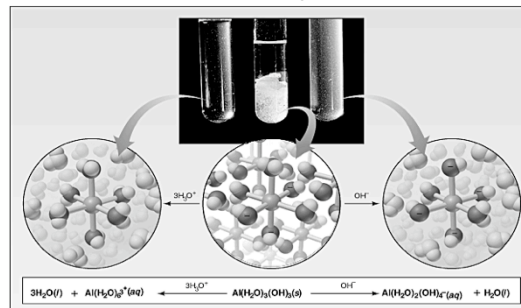
$$x = 3.46 \times 10^{-8}\ M = [Ag(H_2O)_2^+]$$

QUESTION #K.5

As you have seen one method that can increase the solubility of some salts is to form a soluble complex ion. CuS has a K_{sp} of 8.5×10^{-45}. The reaction

$$Cu^{2+}(aq) + 4\,NH_3(aq) \rightarrow Cu(NH_3)_4{}^{2+}$$
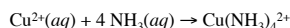
has an equilibrium constant of approximately 5.6×10^{11}. What would be the approximate molar solubility of CuS in a 1.0 M solution of NH_3?

A. $\sim 6.9 \times 10^{-17}$ M
B. $\sim 9.2 \times 10^{-23}$ M
C. $\sim 4.8 \times 10^{-33}$ M
D. The molar solubility would be very, very small, and it is not significant whether the solubility is either A, B, or C.

The Amphoteric Behavior of Aluminum Hydroxide

$$3H_2O(l) + Al(H_2O)_6{}^{3+}(aq) \xrightarrow{3H_3O^+} Al(H_2O)_3(OH)_3(s) \xrightarrow{OH^-} Al(H_2O)_2(OH)_4{}^-(aq) + H_2O(l)$$

Factors That Affect Solubility:

Amphoterism

- Amphoteric oxides will dissolve in either a strong acid or a strong base.
- Examples: hydroxides and oxides of Al^{3+}, Cr^{3+}, Zn^{2+}, and Sn^{2+}.
- The hydroxides generally form complex ions with four hydroxide ligands attached to the metal:

$$Al(OH)_3(s) + OH^-(aq) \rightleftharpoons Al(OH)_4{}^-(aq)$$

- However, hydrated metal ions act as weak acids.

Factors That Affect Solubility:

Amphoterism

- Since hydrated metal ions act as weak acids, the amphoterism is discontinuous (See rxn. #3):

$$Al(H_2O)_6{}^{3+}(aq) + OH^-(aq) \rightleftharpoons Al(H_2O)_5(OH)^{2+}(aq) + H_2O(l)$$

$$Al(H_2O)_5(OH)^{2+}(aq) + OH^-(aq) \rightleftharpoons Al(H_2O)_4(OH)_2{}^+(aq) + H_2O(l)$$

$$Al(H_2O)_4(OH)^+(aq) + OH^-(aq) \rightleftharpoons Al(H_2O)_3(OH)_3(s) + H_2O(l)$$

$$Al(H_2O)_3(OH)_3(s) + OH^-(aq) \rightleftharpoons Al(H_2O)_2(OH)_4{}^-(aq) + H_2O(l)$$

QUESTION #K.6

Given:

$$Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq)$$
$$K_{sp} = 1.6 \times 10^{-19}$$
$$Cu(NH_3)_4{}^{2+} \rightleftharpoons Cu^{2+}(aq) + 4NH_3(aq)$$
$$K = 1.0 \times 10^{-13}$$

What is the value of the equilibrium constant for the reaction:

$$Cu(OH)_2(s) + 4NH_3(aq) \rightleftharpoons Cu(NH_3)_4{}^{2+}(aq) + 2OH^-(aq)$$
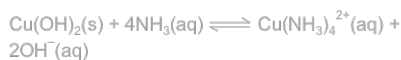
A) 1.6×10^{-19}
B) 6.2×10^{31}
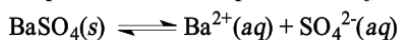C) 1.6×10^{-6}
D) 1.6×10^{-32}

A Sequence of Reactions Affecting Silver Ion Solubilities
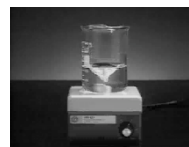
Provide complete net ionic equations (NIEs) for each of the eight silver metal ion reactions in the video (i.e. for each addition) and the respective K_{sp} or K_f value that relates to that particular NIE.

http://chemconnections.org/general/movies/Precip-Equil-I.mov

Precipitation and Separation of Ions

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

- At any instant in time, Q = $[Ba^{2+}][SO_4^{2-}]$.
  - ❖ If $Q > K_{sp}$, precipitation occurs until $Q = K_{sp}$.
  - ❖ If $Q = K_{sp}$, equilibrium exists.
  - ❖ If $Q < K_{sp}$, solid dissolves until $Q = K_{sp}$.
- Based on solubilities, ions can be selectively removed from solutions.
- Consider a mixture of $Zn^{2+}(aq)$ and $Cu^{2+}(aq)$. CuS ($K_{sp} = 6 \times 10^{-37}$) is less soluble than ZnS ($K_{sp} = 2 \times 10^{-25}$), CuS will be removed from solution before ZnS.

Precipitation and Separation of Ions

- As H_2S is added to the green solution, black CuS forms in a colorless solution of $Zn^{2+}(aq)$.
- When more H_2S is added, a second precipitate of white ZnS forms.

Selective Precipitation of Ions

- Ions can be separated from each other based on their salt solubilities.
- Example: if HCl is added to a solution containing Ag^+ and Cu^{2+}, the silver precipitates (K_{sp} for AgCl is 1.8×10^{-10}) while the Cu^{2+} remains in solution.
- Removal of one metal ion from a solution is called *selective precipitation*.

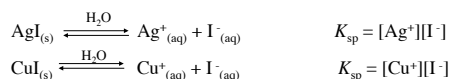## Separating Ions by Selective Precipitation

Problem: A solution consists of 0.10 M AgNO$_3$ and 0.15 M CuNO$_3$.Calculate the [I$^-$] that can be used to separate the metals as their iodides. K_{sp} of AgI = 8.3 x 10^{-17}; K_{sp} of CuI = 1.0 x 10^{-12}.

Plan: Since the two iodides have the same formula type (1:1), directly compare their K_{sp} values. *NOTE: CuI is about 100,000 times more soluble than AgI. Therefore, AgI precipitates first*. Solve for [I$^-$], which is the concentration for a saturated solution of AgI.

Separating Ions by Selective Precipitation

Solution: Writing chemical equations and ion-product expressions:

$$AgI_{(s)} \xrightleftharpoons{H_2O} Ag^+_{(aq)} + I^-_{(aq)} \qquad K_{sp} = [Ag^+][I^-]$$
$$CuI_{(s)} \xrightleftharpoons{H_2O} Cu^+_{(aq)} + I^-_{(aq)} \qquad K_{sp} = [Cu^+][I^-]$$

Calculating the quantity of iodide needed to give a saturated solution of CuI:

$$[I^-] = \frac{K_{sp}}{[Cu^+]} = \frac{1.0 \text{ x } 10^{-12}}{0.10 \ M} = 1.0 \text{ x } 10^{-11} \ M$$

Selective Precipitation

The concentration of iodide ion that will give a saturated solution of copper(I) iodide is 1.0 x 10^{-11} M. This concentration will not precipitate the copper(I) ion. It will remove most of the silver ion. Calculating the quantity of silver ion remaining in solution we get:

$$[Ag^+] = \frac{K_{sp}}{[I^-]} = \frac{8.3 \text{ x } 10^{-17}}{1.0 \text{ x } 10^{-11}} = 8.3 \text{ x } 10^{-6} \ M$$

Since the initial silver ion was 0.10 M, most of it has been removed, and essentially none of the copper(I) was removed, so the separation was quite complete. If the iodide was added as sodium iodide, you would have to add only a few nanograms of NaI to remove nearly all of the silver from solution:

$$1.0 \text{ x } 10^{-11} \text{ mol I}^- \text{ x } \frac{1 \text{ molNaI}}{\text{mol I}^-} \text{ x } \frac{149.9 \text{ g NaI}}{\text{mol NaI}} = 1.50 \text{ ng NaI}$$

Selective Precipitation
Qualitative Analysis:
### *Separating & Identifying Metal Ions*

General Strategy & Procedure for Separating Ions in Qualitative Analysis
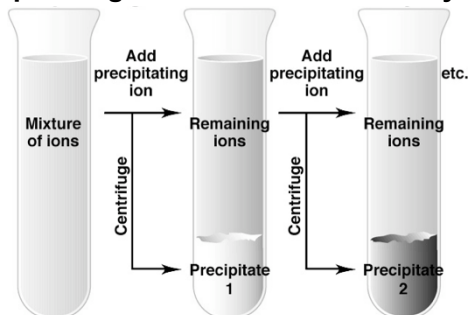

QUESTION #K.7

To separate a solution containing 0.000 10 M silver and 0.10 M lead ions, as done in some qualitative analysis separation schemes, a source of I^- may be slowly added to the mixture of ions. Which will precipitate first: AgI ($K_{sp} = 1.5 \times 10^{-16}$) or PbI_2 ($K_{sp} = 1.4 \times 10^{-8}$)? Also, what would be the concentration of I^- necessary to see that first precipitation?

A. AgI; $[I^-]$ would be 1.5×10^{-12} M
B. AgI; $[I^-]$ would be 1.4×10^{-4} M
C. PbI_2; $[I^-]$ would be 1.4×10^{-7} M
D. PbI_2; $[I^-]$ would be 1.4×10^{-6} M
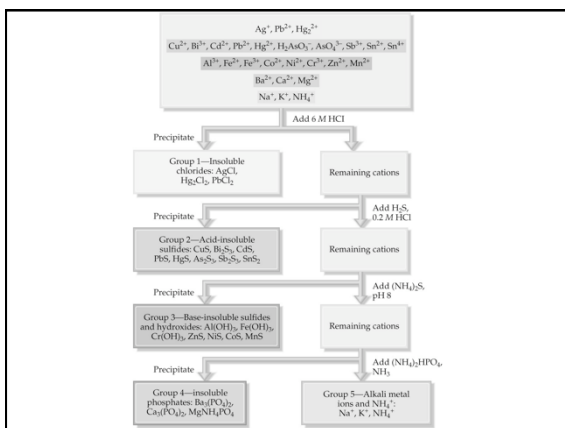
Separation into Ion Groups

Ion Group 1: Insoluble chlorides

$$Ag^+, Hg_2^{2+}, Pb^{2+}$$
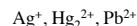
Ion Group 2: Acid-insoluble sulfides

$$Cu^{2+}, Cd^{2+}, Hg^{2+}, As^{3+}, Sb^{3+}, Bi^{3+}, Sn^{2+}, Sn^{4+}, Pb^{2+}$$
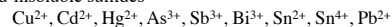
Ion Group 3: Base-insoluble *sulfides* and hydroxides

$$Zn^{2+}, Mn^{2+}, Ni^{2+}, Fe^{2+}, Co^{2+} \text{ as sulfides,}$$
$$\text{and } Al^{3+}, Cr^{3+} \text{ as hydroxides}$$
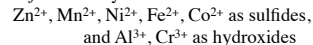
Ion Group 4: Insoluble phosphates

$$Mg^{2+}, Ca^{2+}, Ba^{2+}$$
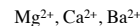
Ion Group 5: Alkali metal and ammonium ions

$$Na^+, K^+, NH_4^+$$
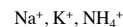
Qualitative Analysis for Separating Cations

A Qualitative Analysis Scheme for Ag^+, Al^{3+}, Cu^{2+} and Fe^{3+}