

# 화학 General Chemistry

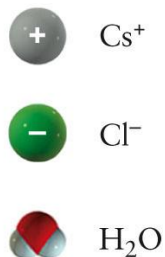
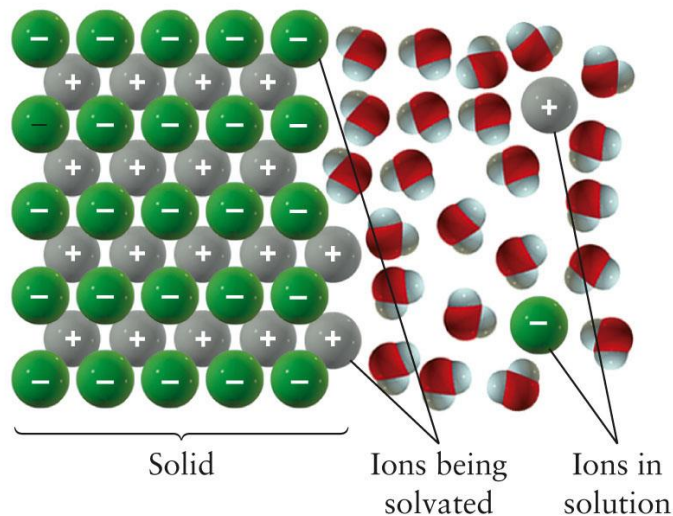
## 034.020-005

2018 Spring Semester

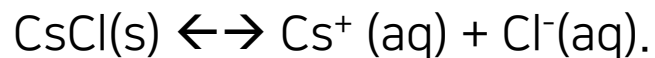
Tue/Thr 9:30~10:45  
Building 028-302

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# What is happening to the ions?



Water molecules surround ions  
="solvation"



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$$K = [\text{Ag}^+][\text{Cl}^-] = K_{\text{sp}} (\text{AgCl}) = 1.6 \times 10^{-10}.$$

Solubility product ( $K_{\text{sp}}$ )

$\text{Ag}_2\text{CrO}_4$  molar solubility at  $25\text{ }^\circ\text{C}$  is  $65\text{ }\mu\text{mol/L}$ .  
What is the  $K_{\text{sp}}$  of  $\text{Ag}_2\text{CrO}_4$  at  $25\text{ }^\circ\text{C}$ ?

$$Q_0 \text{ (reaction quotient)} = [\text{Ag}^+]_0[\text{Cl}^-]_0 \quad \text{AgCl (s)} \rightleftharpoons \text{Ag}^+ \text{ (aq)} + \text{Cl}^- \text{ (aq)}$$

$$K = [\text{Ag}^+][\text{Cl}^-] = K_{sp} (\text{AgCl}) = 1.6 \times 10^{-10}$$

*A salt precipitates if  $Q_{sp}$  is greater than  $K_{sp}$*

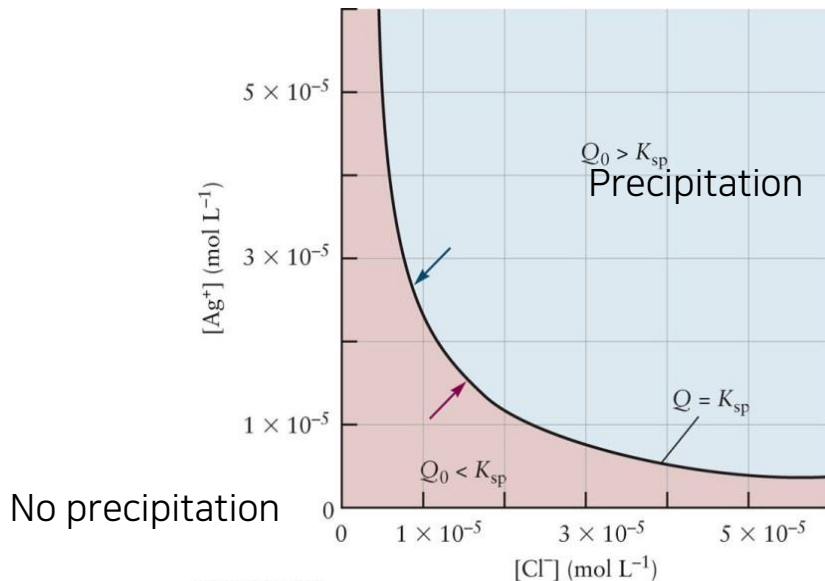
$$[\text{Ag}^+]_0 = 0.0015 \text{ M}$$

$$[\text{Cl}^-]_0 = 5.0 \times 10^{-6} \text{ M}$$

$$Q = [\text{Ag}^+][\text{Cl}^-] = 7.5 \times 10^{-9} > K_{sp}$$

Precipitation occurs!

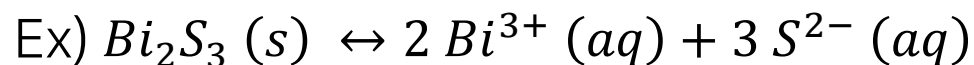
How much remains in solution after the precipitation?



# Solubility Equilibria

## 12.1. The Solubility Product

- Solubility product ( $K_{sp}$ ) in a **saturated solution**



$$K_{sp} \equiv \frac{(a_{Bi^{3+}})^2 \cdot (a_{S^{2-}})^3}{a_{Bi_2S_3}} \approx [Bi^{3+}]^2 \cdot [S^{2-}]^3$$

- $K_{sp}$  is typically used for insoluble or slightly soluble salts: low  $K_{sp}$  values



**TABLE 12.4 Solubility Products at 25°C**

Compound	Formula	$K_{sp}$	Compound	Formula	$K_{sp}$
aluminum hydroxide	$\text{Al}(\text{OH})_3$	$1.0 \times 10^{-33}$	lead(II) fluoride	$\text{PbF}_2$	$3.7 \times 10^{-8}$
antimony sulfide	$\text{Sb}_2\text{S}_3$	$1.7 \times 10^{-93}$	iodate	$\text{Pb}(\text{IO}_3)_2$	$2.6 \times 10^{-13}$
barium carbonate	$\text{BaCO}_3$	$8.1 \times 10^{-9}$	iodide	$\text{PbI}_2$	$1.4 \times 10^{-8}$
fluoride	$\text{BaF}_2$	$1.7 \times 10^{-6}$	sulfate	$\text{PbSO}_4$	$1.6 \times 10^{-8}$
sulfate	$\text{BaSO}_4$	$1.1 \times 10^{-10}$	sulfide	$\text{PbS}$	$8.8 \times 10^{-29}$
bismuth sulfide	$\text{Bi}_2\text{S}_3$	$1.0 \times 10^{-97}$	magnesium ammonium phosphate	$\text{MgNH}_4\text{PO}_4$	$2.5 \times 10^{-13}$
calcium carbonate	$\text{CaCO}_3$	$8.7 \times 10^{-9}$	carbonate	$\text{MgCO}_3$	$1.0 \times 10^{-5}$
fluoride	$\text{CaF}_2$	$4.0 \times 10^{-11}$	fluoride	$\text{MgF}_2$	$6.4 \times 10^{-9}$
hydroxide	$\text{Ca}(\text{OH})_2$	$5.5 \times 10^{-6}$	hydroxide	$\text{Mg}(\text{OH})_2$	$1.1 \times 10^{-11}$
sulfate	$\text{CaSO}_4$	$2.4 \times 10^{-5}$	mercury(I) chloride	$\text{Hg}_2\text{Cl}_2$	$2.6 \times 10^{-18}$
chromium(III) iodate	$\text{Cr}(\text{IO}_3)_3$	$5.0 \times 10^{-6}$	iodide	$\text{Hg}_2\text{I}_2$	$1.2 \times 10^{-28}$
copper(I) bromide	$\text{CuBr}$	$4.2 \times 10^{-8}$	mercury(II) sulfide, black	$\text{HgS}$	$1.6 \times 10^{-52}$
chloride	$\text{CuCl}$	$1.0 \times 10^{-6}$	sulfide, red	$\text{HgS}$	$1.4 \times 10^{-53}$
iodide	$\text{CuI}$	$5.1 \times 10^{-12}$	nickel(II) hydroxide	$\text{Ni}(\text{OH})_2$	$6.5 \times 10^{-18}$
sulfide	$\text{Cu}_2\text{S}$	$2.0 \times 10^{-47}$	silver bromide	$\text{AgBr}$	$7.7 \times 10^{-13}$
copper(II) iodate	$\text{Cu}(\text{IO}_3)_2$	$1.4 \times 10^{-7}$	carbonate	$\text{Ag}_2\text{CO}_3$	$6.2 \times 10^{-12}$
oxalate	$\text{CuC}_2\text{O}_4$	$2.9 \times 10^{-8}$	chloride	$\text{AgCl}$	$1.6 \times 10^{-10}$
sulfide	$\text{CuS}$	$1.3 \times 10^{-36}$	hydroxide	$\text{AgOH}$	$1.5 \times 10^{-8}$
iron(II) hydroxide	$\text{Fe}(\text{OH})_2$	$1.6 \times 10^{-14}$	iodide	$\text{AgI}$	$8 \times 10^{-17}$
sulfide	$\text{FeS}$	$6.3 \times 10^{-18}$	sulfide	$\text{Ag}_2\text{S}$	$6.3 \times 10^{-51}$
iron(III) hydroxide	$\text{Fe}(\text{OH})_3$	$2.0 \times 10^{-39}$	zinc hydroxide	$\text{Zn}(\text{OH})_2$	$2.0 \times 10^{-17}$
lead(II) bromide	$\text{PbBr}_2$	$7.9 \times 10^{-5}$	sulfide	$\text{ZnS}$	$1.6 \times 10^{-24}$
chloride	$\text{PbCl}_2$	$1.6 \times 10^{-5}$			

TABLE 16.2

Solubility Product Constants  $K_{sp}$  at 25°C**Iodates**

AgIO <sub>3</sub>		$[Ag^+][IO_3^-] = 3.1 \times 10^{-8}$
CuIO <sub>3</sub>	-1	$[Cu^+][IO_3^-] = 1.4 \times 10^{-7}$
Pb(IO <sub>3</sub> ) <sub>2</sub>		$[Pb^{2+}][IO_3^-]^2 = 2.6 \times 10^{-13}$

**Carbonates**

Ag <sub>2</sub> CO <sub>3</sub>		$[Ag^+]^2[CO_3^{2-}] = 6.2 \times 10^{-12}$
BaCO <sub>3</sub>		$[Ba^{2+}][CO_3^{2-}] = 8.1 \times 10^{-9}$
CaCO <sub>3</sub>		$[Ca^{2+}][CO_3^{2-}] = 8.7 \times 10^{-9}$
PbCO <sub>3</sub>	-2	$[Pb^{2+}][CO_3^{2-}] = 3.3 \times 10^{-14}$
MgCO <sub>3</sub>		$[Mg^{2+}][CO_3^{2-}] = 4.0 \times 10^{-5}$
SrCO <sub>3</sub>		$[Sr^{2+}][CO_3^{2-}] = 1.6 \times 10^{-9}$

**Chromates**

Ag <sub>2</sub> CrO <sub>4</sub>		$[Ag^+]^2[CrO_4^{2-}] = 1.9 \times 10^{-12}$
BaCrO <sub>4</sub>	-2	$[Ba^{2+}][CrO_4^{2-}] = 2.1 \times 10^{-10}$
PbCrO <sub>4</sub>		$[Pb^{2+}][CrO_4^{2-}] = 1.8 \times 10^{-14}$

**Oxalates**

CuC <sub>2</sub> O <sub>4</sub>		$[Cu^{2+}][C_2O_4^{2-}] = 2.9 \times 10^{-8}$
FeC <sub>2</sub> O <sub>4</sub>		$[Fe^{2+}][C_2O_4^{2-}] = 2.1 \times 10^{-7}$
MgC <sub>2</sub> O <sub>4</sub>	-2	$[Mg^{2+}][C_2O_4^{2-}] = 8.6 \times 10^{-5}$
PbC <sub>2</sub> O <sub>4</sub>		$[Pb^{2+}][C_2O_4^{2-}] = 2.7 \times 10^{-11}$
SrC <sub>2</sub> O <sub>4</sub>		$[Sr^{2+}][C_2O_4^{2-}] = 5.6 \times 10^{-8}$

**Sulfates**

BaSO <sub>4</sub>		$[Ba^{2+}][SO_4^{2-}] = 1.1 \times 10^{-10}$
CaSO <sub>4</sub>	-2	$[Ca^{2+}][SO_4^{2-}] = 2.4 \times 10^{-5}$
PbSO <sub>4</sub>		$[Pb^{2+}][SO_4^{2-}] = 1.1 \times 10^{-8}$

**Fluorides**

BaF <sub>2</sub>		$[Ba^{2+}][F^-]^2 = 1.7 \times 10^{-6}$
CaF <sub>2</sub>	-1	$[Ca^{2+}][F^-]^2 = 3.9 \times 10^{-11}$
MgF <sub>2</sub>		$[Mg^{2+}][F^-]^2 = 6.6 \times 10^{-9}$
PbF <sub>2</sub>		$[Pb^{2+}][F^-]^2 = 3.6 \times 10^{-8}$
SrF <sub>2</sub>		$[Sr^{2+}][F^-]^2 = 2.8 \times 10^{-9}$

**Chlorides**

AgCl		$[Ag^+][Cl^-] = 1.6 \times 10^{-10}$
CuCl	-1	$[Cu^+][Cl^-] = 1.0 \times 10^{-6}$
Hg <sub>2</sub> Cl <sub>2</sub>		$[Hg_2^{2+}][Cl^-]^2 = 1.2 \times 10^{-18}$

**Bromides**

AgBr		$[Ag^+][Br^-] = 7.7 \times 10^{-13}$
CuBr	-1	$[Cu^+][Br^-] = 4.2 \times 10^{-8}$
Hg <sub>2</sub> Br <sub>2</sub>		$[Hg_2^{2+}][Br^-]^2 = 1.3 \times 10^{-21}$

**Iodides**

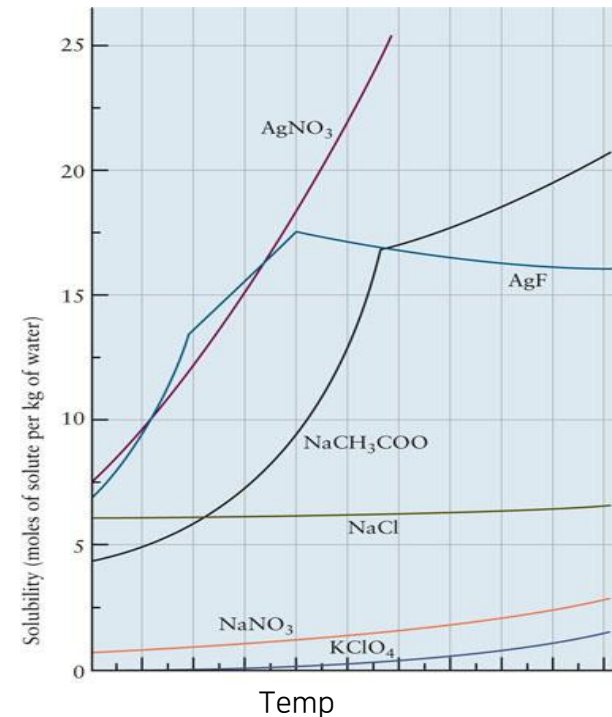
AgI		$[Ag^+][I^-] = 1.5 \times 10^{-16}$
CuI	-1	$[Cu^+][I^-] = 5.1 \times 10^{-12}$
PbI <sub>2</sub>		$[Pb^{2+}][I^-]^2 = 1.4 \times 10^{-8}$
Hg <sub>2</sub> I <sub>2</sub>		$[Hg_2^{2+}][I^-]^2 = 1.2 \times 10^{-28}$

**Hydroxides**

AgOH		$[Ag^+][OH^-] = 1.5 \times 10^{-8}$
Al(OH) <sub>3</sub>		$[Al^{3+}][OH^-]^3 = 3.7 \times 10^{-15}$
Fe(OH) <sub>3</sub>		$[Fe^{3+}][OH^-]^3 = 1.1 \times 10^{-36}$
Fe(OH) <sub>2</sub>	-1	$[Fe^{2+}][OH^-]^2 = 1.6 \times 10^{-14}$
Mg(OH) <sub>2</sub>		$[Mg^{2+}][OH^-]^2 = 1.2 \times 10^{-11}$
Mn(OH) <sub>2</sub>		$[Mn^{2+}][OH^-]^2 = 2.0 \times 10^{-13}$
Zn(OH) <sub>2</sub>		$[Zn^{2+}][OH^-]^2 = 4.5 \times 10^{-17}$

# Solubility of ionic solids

- **Molar solubility**  
= Moles of solids that can maximally dissolve in 1 liter of water
- **Gram solubility**  
= grams of solids that can dissolve in 1 liter of water.
- Solubilities of most of ionic salts increase with T.
- The changes are not smooth because different solid hydrates form over different temperature ranges.
- Typically when the solubility at 25 °C is less than 0.1g/L: insoluble. More than 10g/L: soluble.



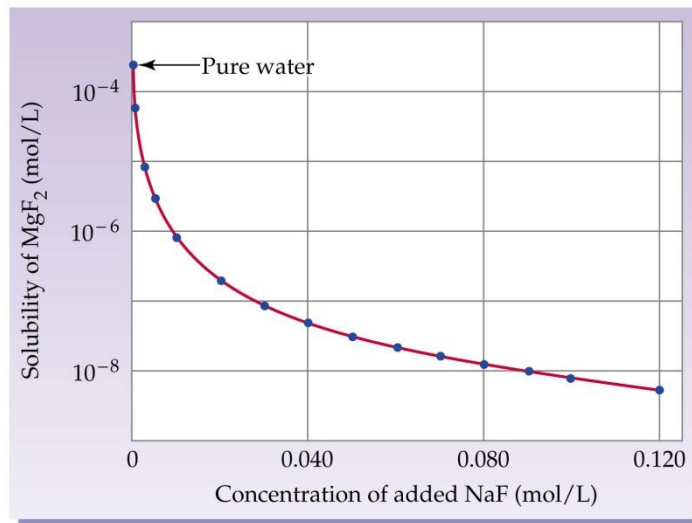
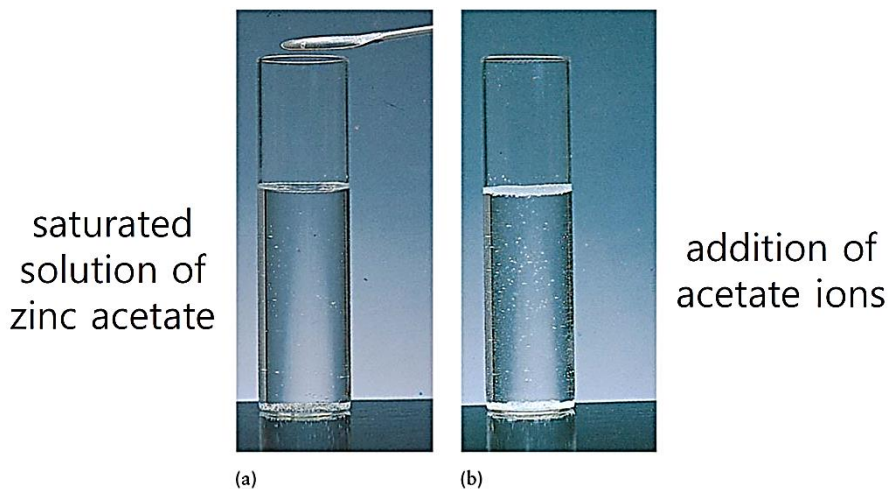


## 12.2. The Common-Ion Effects

- Common-Ion Effect: the suppression of the degree of dissociation of a weak electrolyte containing a common ion according to Le Chatelier's principle.

### Example

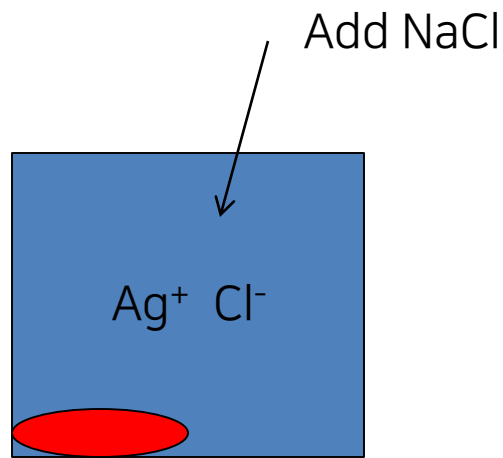
Estimate the solubility of  $\text{AgCl}$  in  $10^{-4} \text{ M NaCl (aq)}$  at  $25^\circ \text{C}$ .



# Common ion effect

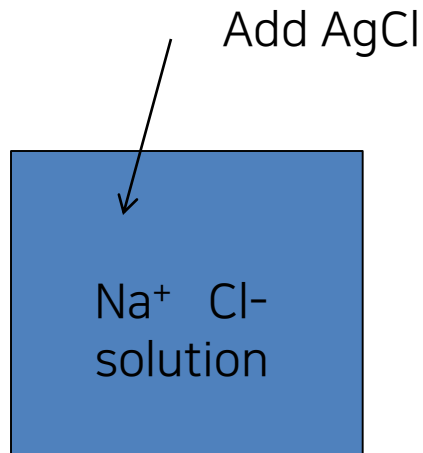


if there's already some amount of common ion in the solution, the solubility is **further reduced**.

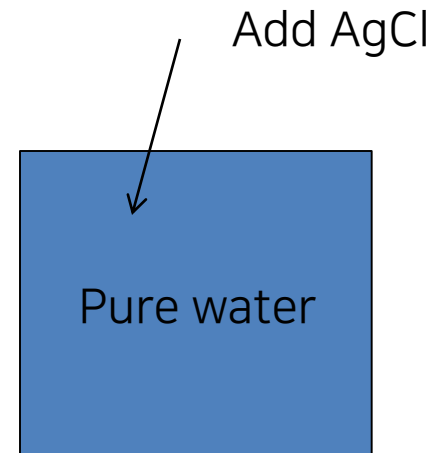


$\text{AgCl(s)}$

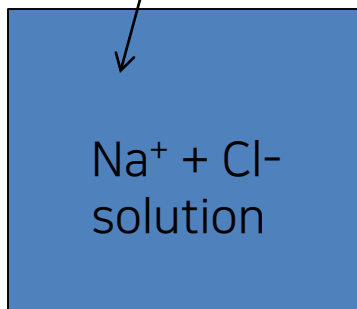
More AgCl precipitates



Earlier precipitation



Add AgCl



0.1 M, 1 liter, NaCl solution

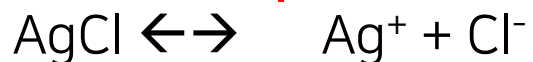
Amount of AgCl that can dissolve = x.

$$[\text{Ag}^+]_{\text{eq}} =$$

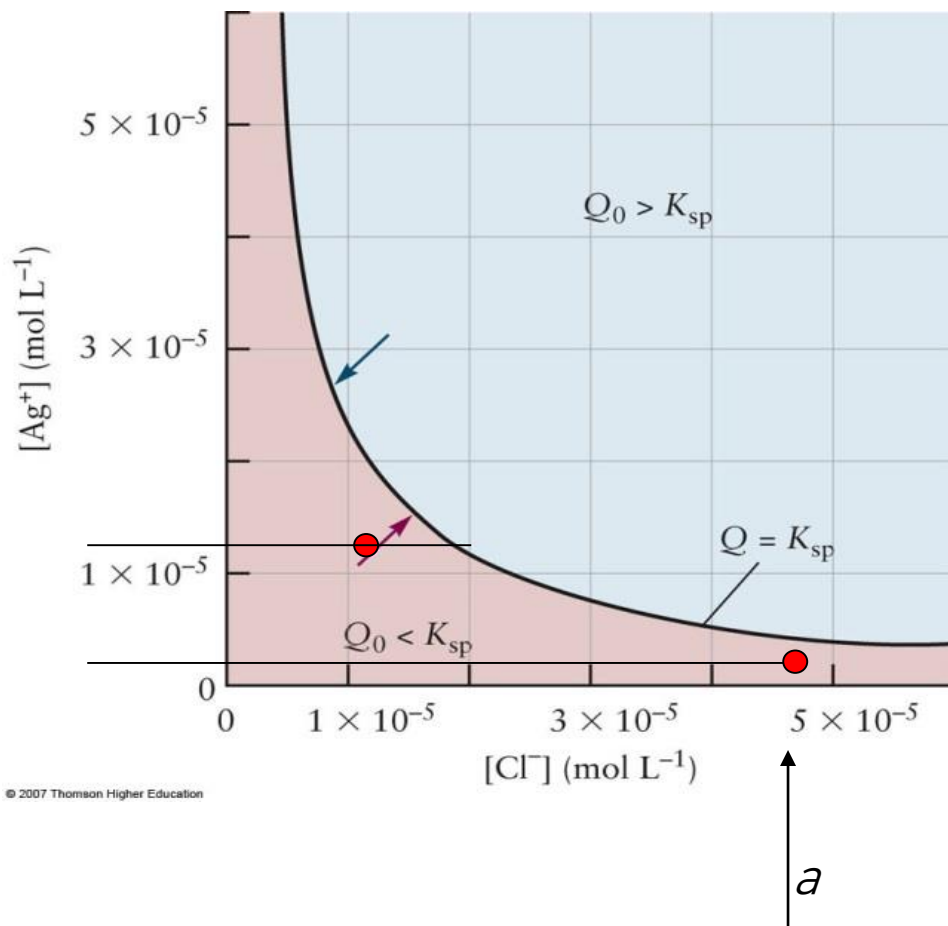
$$, [\text{Cl}^-]_{\text{eq}} =$$

Addition of AgCl onto pure water:

## Dominant equilibrium in precipitation reactions:

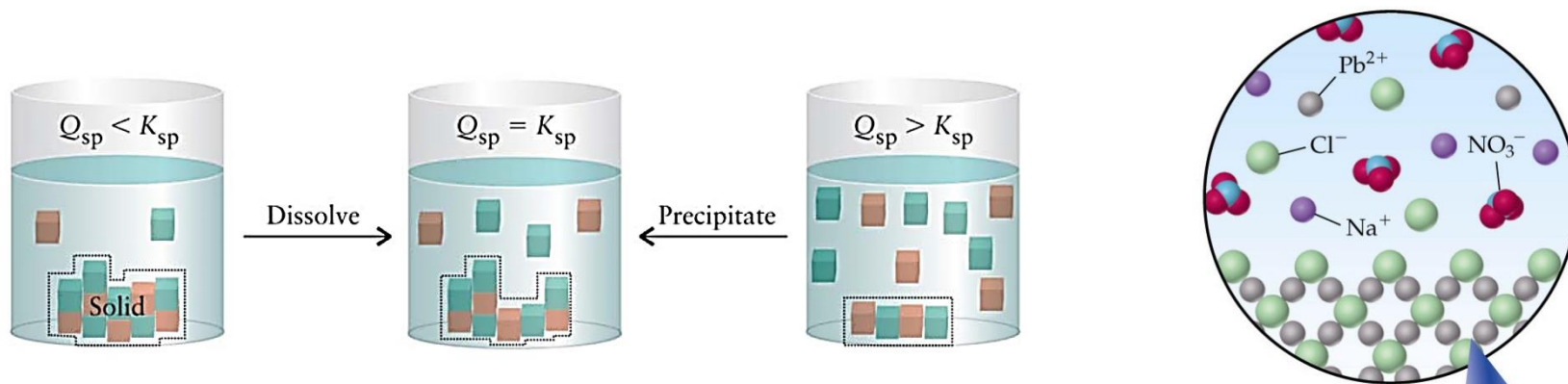


$[\text{Cl}^-]$  is determined by the amount  $a$  of NaCl we put in.



## 12.3. Predicting Precipitation

- If  $Q_{sp}$  is greater than  $K_{sp}$ , then a salt precipitates.



### Example.

When 0.150 L of 0.10 M  $Pb(NO_3)_2$  (aq) and 0.100 L of 0.20 M NaCl are mixed. Will lead(II) chloride,  $PbCl_2$  precipitate?



## 12.4. Selective Precipitation

- Separation of different **cations** in solution

: add a soluble salt containing an **anion** with which the cation form insoluble salts.

→ If the insoluble salts have sufficiently different solubilities, they will precipitate at different anion concentrations and can be collected separately.

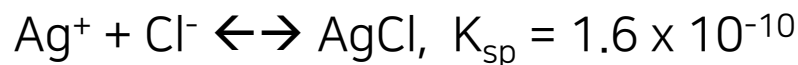
### Example

A sample of seawater contains  $0.050 \text{ mol/L Mg}^{2+} (\text{aq})$  and  $0.010 \text{ mol/L Ca}^{2+} (\text{aq})$ . (a) Determine the order in which ion precipitates as solid NaOH is added, and give the concentration of  $\text{OH}^-$  when precipitation of each begins. (b) Calculate the concentration of the first ion when the second one starts to precipitate.

# Selective precipitation

Mixture of lead and silver ions → We want to separate Pb and Ag ions

Addition of x-M of Cl<sup>-</sup>:



Add NaCl

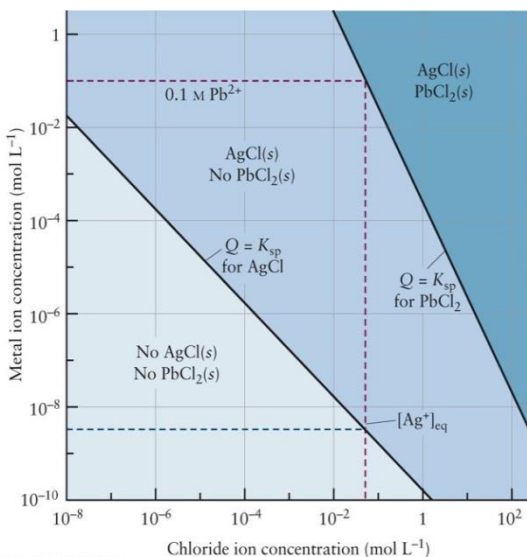
0.1 M Pb<sup>2+</sup>

0.1 M Ag<sup>+</sup>

*What is the appropriate amount of Cl<sup>-</sup> that will precipitate nearly all of Ag<sup>+</sup> while keeping all of the Pb<sup>2+</sup> in solution?*

Maximum conc. of Cl<sup>-</sup> before the PbCl<sub>2</sub> precipitation is:

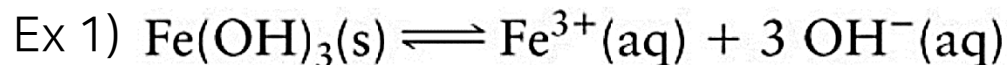
At this [Cl<sup>-</sup>], the amount of Ag<sup>+</sup> ions remaining is:



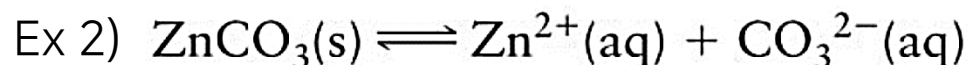
## 12.5. Dissolving Precipitates

### - Ion removal

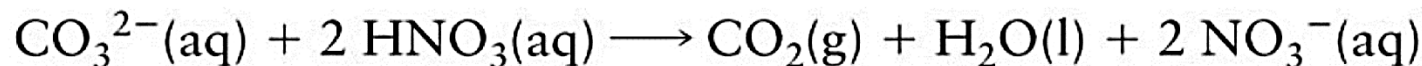
: A precipitate will dissolve if one of the ions in the solubility equilibrium are removed.



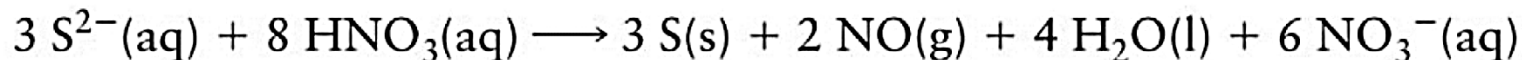
Adding acid to remove the  $\text{OH}^{-}$  ions



Adding nitric acid to form  $\text{CO}_2$



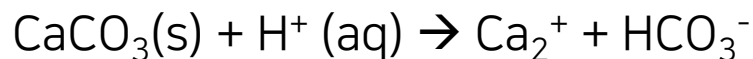
Adding nitric acid to form S





# Effect of pH on solubility

Some solids are only weakly soluble in water but dissolve readily in **acidic solutions**.



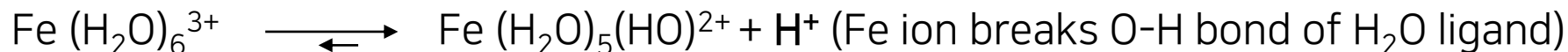
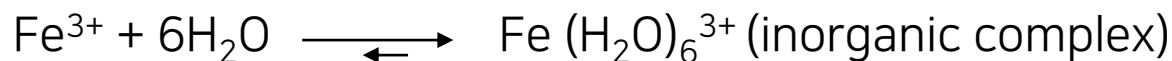
\* Solubility of **metal hydroxides** depends on pH



In pure water,

If the solution is **buffered** at pH = 6,

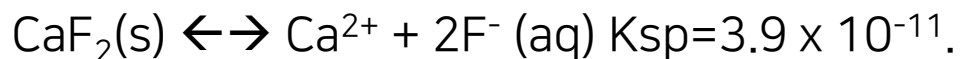
# Some metal ions react with water molecules



**TABLE 16.5** pH of 0.1 M  
Aqueous Metal Nitrate  
Solutions at 25°C

Metal Nitrate	PH
$\text{Fe}(\text{NO}_3)_3$	1.6
$\text{Pb}(\text{NO}_3)_2$	3.6
$\text{Cu}(\text{NO}_3)_2$	4.0
$\text{Zn}(\text{NO}_3)_2$	5.3
$\text{Ca}(\text{NO}_3)_2$	6.7
$\text{NaNO}_3$	7.0

If the ions are conjugate bases of weak acids,



The  $\text{F}^-$  can react with  $\text{H}^+$ :

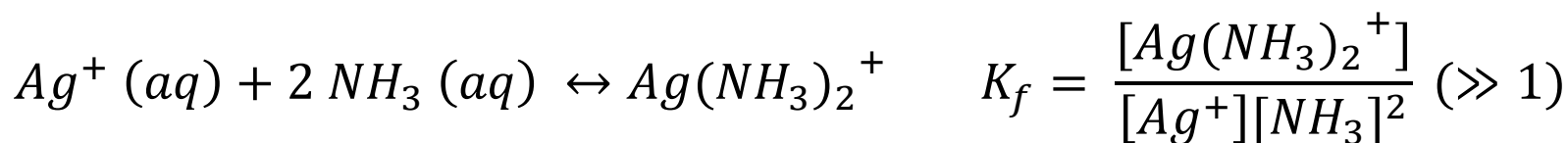


The same thing does not happen to  $\text{CaCl}_2$ . Why?



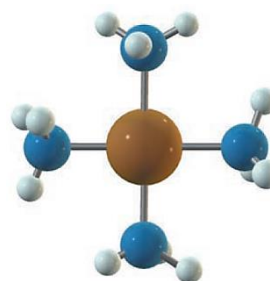
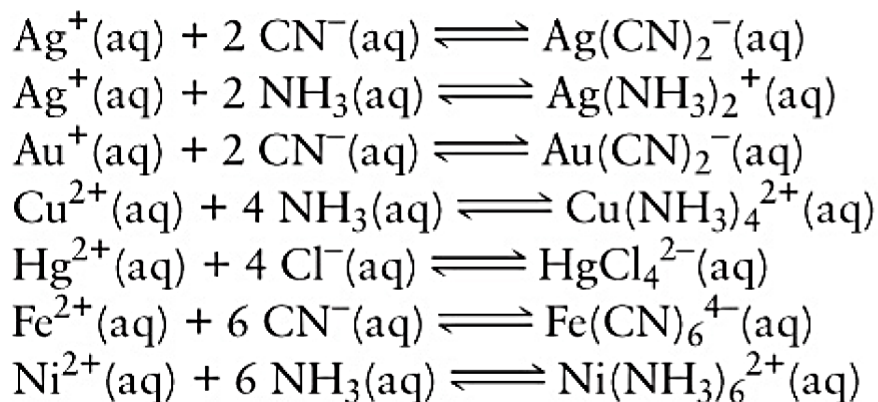
## 12.6. Complex Ion Formation

- Coordination Complex
- The solubility of the salt is increased by the complex ion formation.



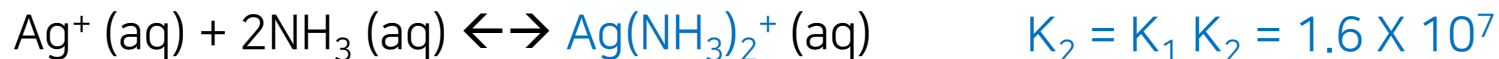
$K_f$ : formation constant

### Equilibrium



$$\begin{aligned} &5.6 \times 10^8 \\ &1.6 \times 10^7 \\ &2.0 \times 10^{38} \\ &1.2 \times 10^{13} \\ &1.2 \times 10^5 \\ &7.7 \times 10^{36} \\ &5.6 \times 10^8 \end{aligned}$$

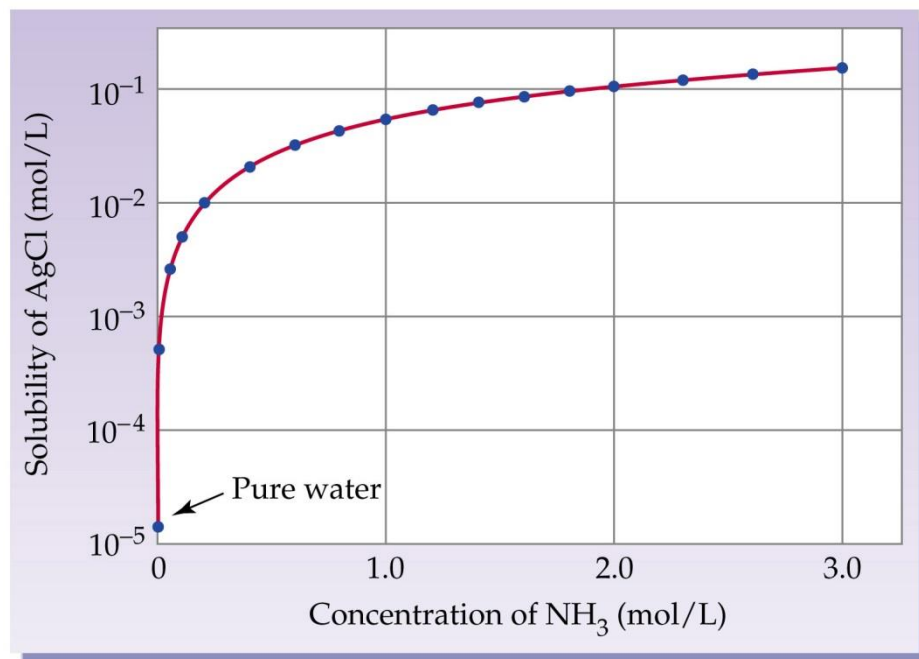
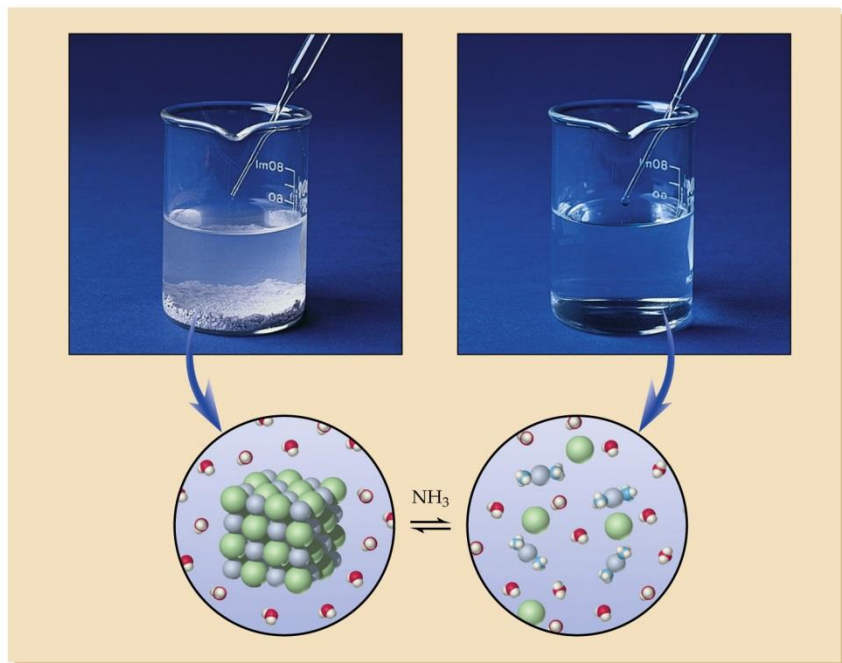
# Complexation Equilibrium



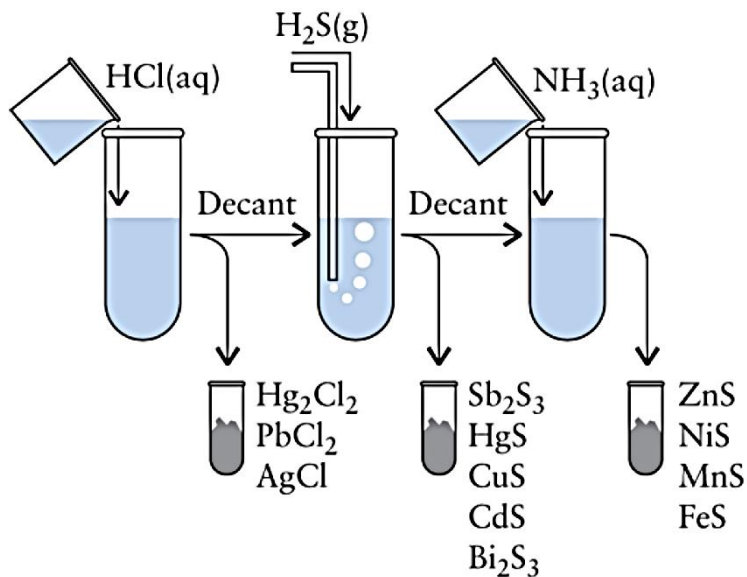
Solubility of  $\text{AgBr}$  in ammonia solution is greatly increased by the addition of ligands.

Solubility of  $\text{AgBr}$  in 1.00 M ammonia solution?

Molar solubility of AgCl in 0.10 M  $\text{NH}_3$  (aq) solution.



# 12.7. Qualitative Analysis



Step	Possible precipitate	$K_{sp}$
1) Add $\text{HCl(aq)}$	$\text{AgCl}$	$1.6 \times 10^{-10}$
	$\text{Hg}_2\text{Cl}_2$	$1.3 \times 10^{-18}$
	$\text{PbCl}_2$	$1.6 \times 10^{-5}$
2) Add $\text{H}_2\text{S(aq)}$ (in acid solution, there is a low $\text{S}^{2-}$ concentration)	$\text{Bi}_2\text{S}_3$	$1.0 \times 10^{-97}$
	$\text{CdS}$	$4.0 \times 10^{-29}$
	$\text{CuS}$	$7.9 \times 10^{-45}$
	$\text{HgS}$	$1.6 \times 10^{-52}$
	$\text{Sb}_2\text{S}_3$	$1.6 \times 10^{-93}$
3) Add base to $\text{H}_2\text{S(aq)}$ (in basic solution, there is a higher $\text{S}^{2-}$ concentration)	$\text{FeS}$	$6.3 \times 10^{-18}$
	$\text{MnS}$	$1.3 \times 10^{-15}$
	$\text{NiS}$	$1.3 \times 10^{-24}$
	$\text{ZnS}$	$1.6 \times 10^{-24}$

