Effect of pH

If the Compound Contains a(n):

- **Basic Anion:** More soluble in acidic solution

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

In acidic solution: $OH^-(aq) + H_3O^+(aq) \rightleftharpoons 2H_2O(l)$

OH^- removed from solution, dissolution equilibrium shifts toward more dissolved product

- **Acidic Cation:** More soluble in basic solution

$$C_7H_7OCOOH(s) \rightleftharpoons C_7H_7OCOO^-(aq) + H_3O^+(aq)$$

In basic solution: $OH^-(aq) + H_3O^+(aq) \rightleftharpoons 2H_2O(l)$

H_3O^+ removed from solution, dissolution equilibrium shifts toward more dissolved product

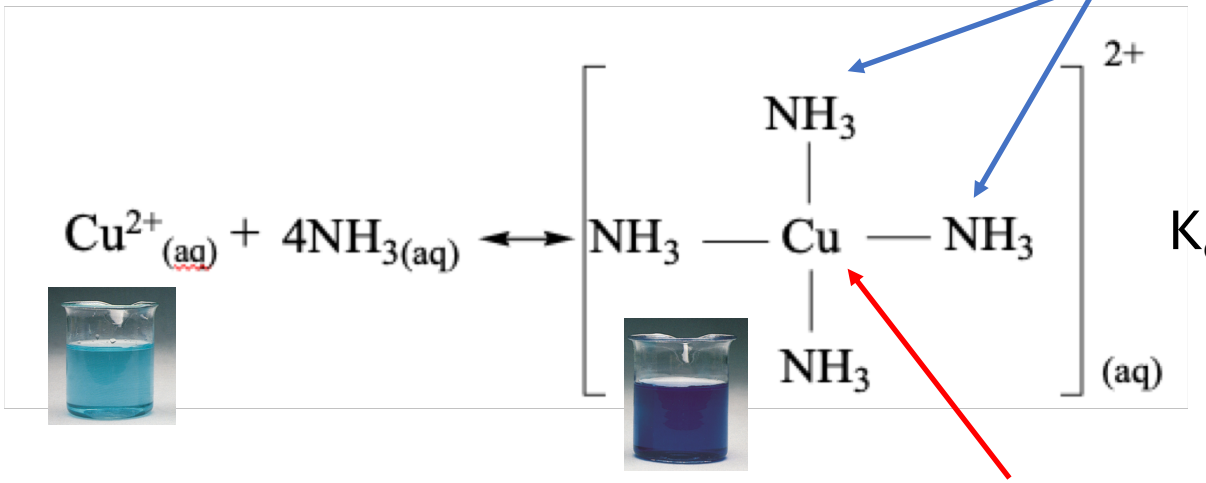
Effect of pH Calculations

Calculate the solubility of $Mg(OH)_2$ (one of the ingredients in the antacid Maalox) in grams per liter when buffered at pH: (a) 12.50; (b) 7.00 A: a.) 7.01×10^{-7} g/L; b.) 7.00×10^{4} g/L

K_{sp} of $Mg(OH)_2 = 1.2 \times 10^{-11}$; MM $Mg(OH)_2 = 58.32$ g/mol

Complex Ion Formation

Complex Ion: A central metal ion surrounded by other groups (molecules or ions) called **ligands**.



$$K_{eq} = K_f = \frac{[Cu(NH_3)_4{}^{2+}]}{[Cu^{2+}][NH_3]^4}$$

The metal center (Cu) is a Lewis Acid that accepts electron pairs from the ligands (NH_3), which act as Lewis Bases by donating electron pairs.

Formation of a complex ion is a reversible equilibrium reaction with its own equilibrium constant, K_f.

K_f = formation constant

Common Complex Ion Ligands: NH_3, CN^-, OH^-, Br^-, I^-

K_f Values for Selected Complex Ions

TABLE 17.4 Formation Constants of Selected Complex Ions in Water at 25°C

Complex Ion	Equilibrium Expression	Formation Constant (K_f)
$Ag(NH_3)_2^+$	$Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+$	1.5×10^7
$Ag(CN)_2^-$	$Ag^+ + 2CN^- \rightleftharpoons Ag(CN)_2^-$	1.0×10^{21}
$Cu(CN)_4^{2-}$	$Cu^{2+} + 4CN^- \rightleftharpoons Cu(CN)_4^{2-}$	1.0×10^{25}
$Cu(NH_3)_4^{2+}$	$Cu^{2+} + 4NH_3 \rightleftharpoons Cu(NH_3)_4^{2+}$	5.0×10^{13}
$Cd(CN)_4^{2-}$	$Cd^{2+} + 4CN^- \rightleftharpoons Cd(CN)_4^{2-}$	7.1×10^{16}
CdI_4^{2-}	$Cd^{2+} + 4I^- \rightleftharpoons CdI_4^{2-}$	2.0×10^6
$HgCl_4^{2-}$	$Hg^{2+} + 4Cl^- \rightleftharpoons HgCl_4^{2-}$	1.7×10^{16}
HgI_4^{2-}	$Hg^{2+} + 4I^- \rightleftharpoons HgI_4^{2-}$	2.0×10^{30}
$Hg(CN)_4^{2-}$	$Hg^{2+} + 4CN^- \rightleftharpoons Hg(CN)_4^{2-}$	2.5×10^{41}
$Co(NH_3)_6^{3+}$	$Co^{3+} + 6NH_3 \rightleftharpoons Co(NH_3)_6^{3+}$	5.0×10^{31}
$Zn(NH_3)_4^{2+}$	$Zn^{2+} + 4NH_3 \rightleftharpoons Zn(NH_3)_4^{2+}$	2.9×10^9

Complex Ion Formation & Solubility

Formation of a Complex Ion can increase solubility

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \qquad K_{sp}$$

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

$$AgCl(s) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) + Cl^-(aq) \qquad K_c$$

- Ag^+ is removed from solution, shifting solubility equilibrium to the dissociated products
- More AgCl(s) dissolves
- K_{sp} governs first process
- K_f governs second process
- Two processes are added together
- K_c (overall equilibrium expression) = K_{sp} x K_f

Complex Ion Formation & Solubility

1. Determine the equilibrium constant for the reaction:

$$AgI(s) + 2CN^-(aq) \rightleftharpoons Ag(CN)_2^-(aq) + I^-(aq)$$

$$K_{sp}\ AgI = 8.3 \times 10^{-17};\ K_f\ Ag(CN)_2^- = 1 \times 10^{21}$$

A: 8×10^4

Complex Ion Formation & Solubility

2. Calculate the molar solubility of zinc carbonate at 25°C in (a) pure water and (b) 1.0M NH_3
$K_{sp} = 1.4 \times 10^{-11}$; $K_f = 4.1 \times 10^{8}$

A: (a) 3.7×10^{-6}
(b) 7.6×10^{-2}

Prediction of Precipitation

Whether or not a precipitate will form depends on concentration.

Can use Q_c values to predict precipitate formation

Calculate Q_c based on given concentrations & compare Q_c to K_{sp}

- $Q_c > K_{sp}$ Concentration too high → Precipitate will form
- $Q_c < K_{sp}$ Concentration low → all ions remain in solution
- $Q_c = K_{sp}$ At Equilibrium → saturated solution

Prediction of Precipitation

1.) If 2.00mL of 0.200M NaOH are added to 1.00L of 0.100M $CaCl_2$, will a precipitate form? A: no precipitate will form

Prediction of Precipitation

2.) How many grams of solid K_2SO_4 (174.3g/mol) would need to be added to 50.0mL of a 0.0010M $Ca(NO_3)_2$ solution in order to (a) start precipitation and (b) precipitate 99% of the calcium?

A: 0.079g

Prediction of Precipitation

2.) How many grams of solid K_2SO_4 (174.3g/mol) would need to be added to 50.0mL of a 0.0010M $Ca(NO_3)_2$ solution in order to (a) start precipitation and (b) precipitate 99% of the calcium?

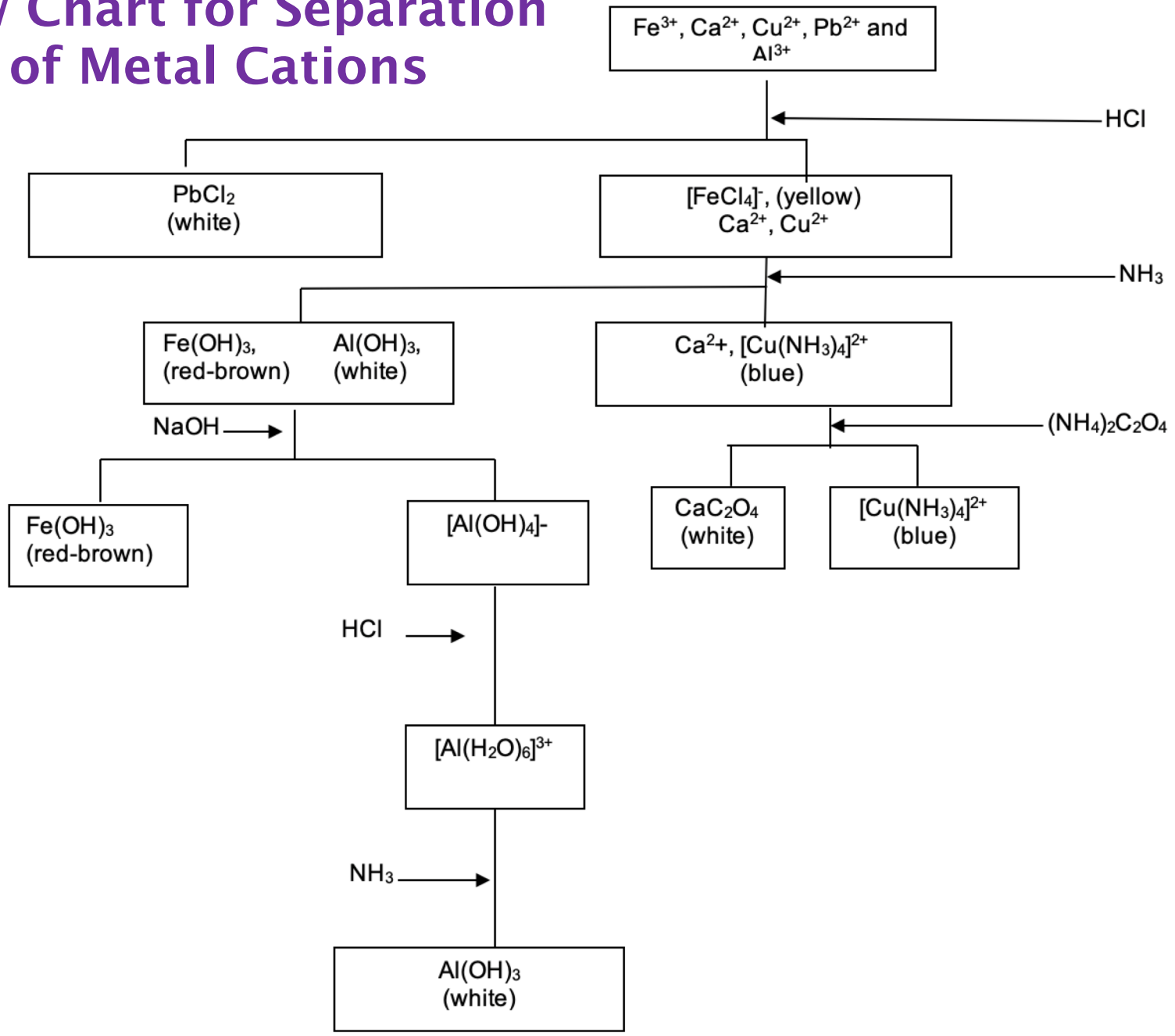
A: 7.9g

Qualitative Analysis of Metal Ions

Ways to determine which ions are present in solution

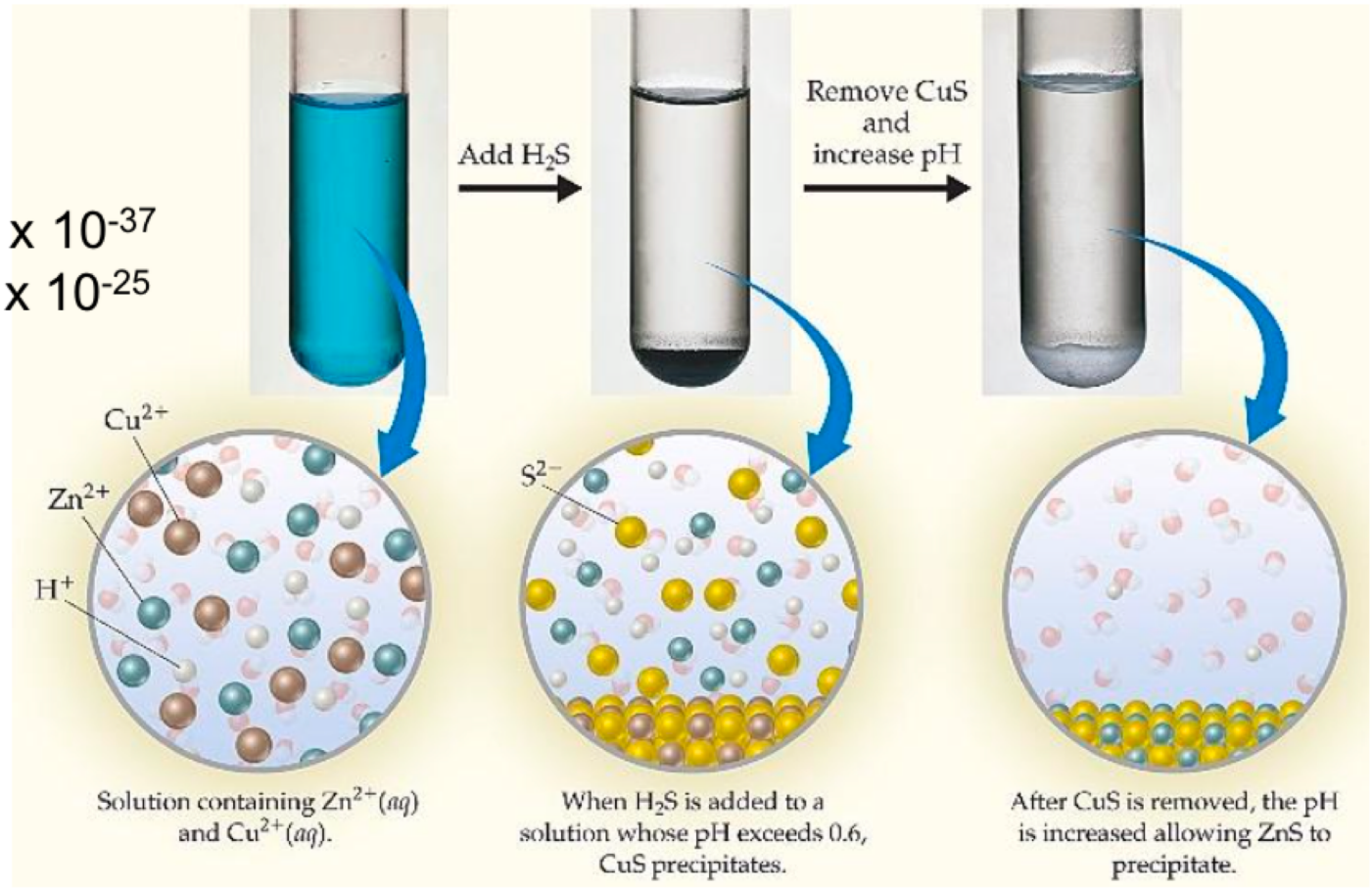
- **Selective precipitation**
  - One compound has very low K_{sp} and will form a precipitate
  - Other compounds have very high (or no) K_{sp}
- **Complex formation**
  - Ligands will only form complex with one ion present
  - May cause a precipitate to dissolve
- **Flame tests**
  - Color of flame can be used for ID
  - CHM 101 – energy levels!

Flow Chart for Separation of Metal Cations



Selective Precipitation

K_{sp}:
$CuS = 6 \times 10^{-37}$
$ZnS = 2 \times 10^{-25}$



Solution contains $Zn^{2+}(aq)$ & $Cu^{2+}(aq)$

H_2S is added
At low pH (but > 0.6)
CuS precipitates

CuS is removed then pH is increased causing ZnS to precipitate

Selective Precipitation

A solution contains 0.050M Mg^{2+} and 0.020M Cu^{2+}. Solid NaOH is added to the solution. K_{sp} $Mg(OH)_2 = 1.8x10^{-11}$; K_{sp} $Cu(OH)_2 = 4.8x10^{-20}$

(a) Which ion will precipitate first? A: Cu^{2+}

(b) What concentration of OH^- is necessary to begin precipitation of each cation. A: Cu^{2+} needs $1.5x10^{-9}$M
Mg^{2+} needs $1.9x10^{-5}$M