Grade 12 Chemistry

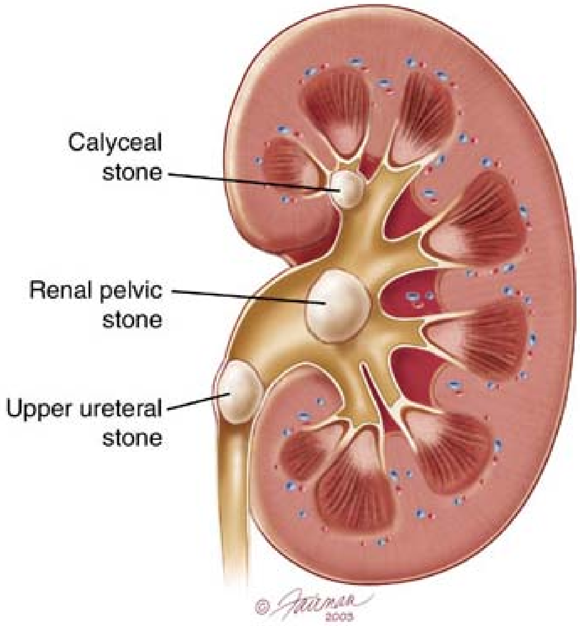
Chemical Systems & Equilibrium

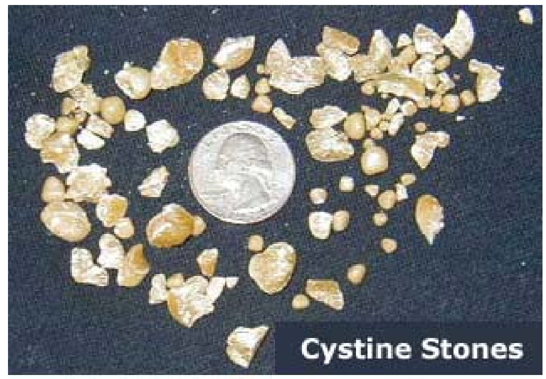
Class 14

Kidney Stones

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

- This reaction is controlled by the kidney and must be in equilibrium at all times
- If the kidneys remove too much phosphate, calcium phosphate in the bone is broken down leading to osteoporosis
- If kidneys retain too much calcium, solid calcium precipitates producing kidney stones





Solubility Product Constant

- When do you know a solution is in equilibrium? When excess solid is present in the saturated solution
- The extent to which a salt will dissolve in water can be determined from its solubility product constant, K_{sp}

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

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

- When a salt dissolves, the entropy of the system always increases because ions in solution are more disordered than ions in a solid crystal (ΔS is positive; -TΔS becomes more negative)

- K_{sp} is temperature-dependent and different experiments needs to be carried out to determine K_{sp} at different temperatures

Checkpoint

A chemist finds that molar solubility of silver carbonate, Ag_2CO_3 is 1.3×10^{-4}M at 25°C. Calculate the K_{sp} for silver carbonate.

Solubility

- **Solubility** – the number of *grams* of solute in 1L of saturated solution (g/L)
- **Molar Solubility** - The number of *moles* of solute in 1L of a saturated solution (mol/L)

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

$$x \leftrightarrows x + 2x$$

Where x = number of moles of $Mg(OH)_2$ that have dissolved in 1L of saturated solution

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

$$K_{sp} = [x][2x]^2$$

$$K_{sp} = 4x^3$$

From experimental values: $K_{sp} = 1.6 \times 10^{-11}$

$$1.6 \times 10^{-11} = 4x^3$$

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

This means that a solution of $Mg(OH)_2$ at 25°C will be saturated at a $[Mg(OH)_2]$ of 1.6×10^{-4} mol/L

Table 9.2 Values of K_{sp} for Some Ionic Compounds at 25°C

Compound	K_{sp}
magnesium sulfate, $MgSO_4$	5.9×10^{-3}
lead(II) chloride, $PbCl_2$	1.7×10^{-5}
barium fluoride, BaF_2	1.5×10^{-6}
cadmium carbonate, $CdCO_3$	1.8×10^{-14}
copper(II) hydroxide, $Cu(OH)_2$	2.2×10^{-20}
silver sulfide, Ag_2S	8×10^{-48}

Checkpoint

What is the molar solubility of PbI_2 in water at 25°C? $K_{sp} = 9.8 \times 10^{-9}$

The Common Ion Effect

$NaF(s) \leftrightarrows Na^{+}(aq) + F^{-}(aq)$

If we add NaF(s) into a solution that contains MgF_2, then we add F^{-}, thereby shifting the equilibrium to the left

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

The result is that MgF_2 precipitates out.

Checkpoint

Calculate the molar solubility of MgF_2 in 0.10M of NaF at 25°C. K_{sp} of $MgF_2 = 7.4 \times 10^{-11}$

Checkpoint

The solubility of pure $PbCrO_4$(s) in water is 4.8×10^{-7} mol/L.

a) Qualitatively predict how the solubility will change if $PbCrO_4$(s) is added to a 0.10 mol/L solution of sodium chromate, Na_2CrO_4

b) K_{sp} for $PbCrO_4$(s) is 2.3×10^{-13}. Determine the solubility of $PbCrO_4$(s) in a 0.10 mol/L solution of Na_2CrO_4

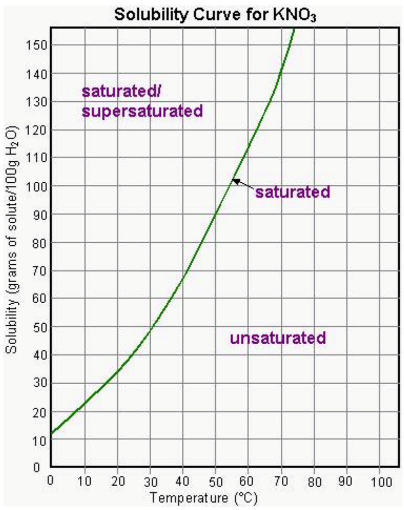
Predicting the Precipitate

Table 9.1 General Solubility Guidelines

Guideline	Cations	Anions	Result	Exceptions
1	Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+	NO_3^-, CH_3COO^-, ClO_3^-	soluble	$Ca(ClO_3)_2$ is insoluble
2	Ag^+, Pb^{2+}, Hg^+	CO_3^{2-}, PO_4^{3-}, O^{2-}, S^{2-}, OH^-	insoluble	BaO and $Ba(OH)_2$ are soluble. Group 2 sulfides tend to decompose.
3		Cl^-, Br^-, I^-	soluble	
4	Ba^{2+}, Ca^{2+}, Sr^{2+}		insoluble	
5	Mg^{2+}, Cu^{2+}, Zn^{2+}, Fe^{2+}, Fe^{3+}, Al^{3+}	SO_4^{2-}	soluble	

- Does not tell us how much will dissolve; need a quantitative approach

Ion Product Q_{sp}



- For the dissolution of any ionic solid, any one of the following may exist:
  1. The solution is unsaturated **($Q_{sp} < K_{sp}$)**
  2. The solution is saturated **($Q_{sp} = K_{sp}$)**
  3. The solution is supersaturated **($Q_{sp} > K_{sp}$)**; precipitate forms

Checkpoint

A chemist mixes 100.0 mL of 0.25 mol/L $Ca(NO_3)_2$ with 200.0 mL of 0.070 mol/L NaF. Does a precipitate form? K_{sp} for CaF_2 is 3.2×10^{-11}.

Analytical Applications of Precipitation Reactions

- Used to remove ions from solution or to identify ions in a unknown solution

Fractional Precipitation

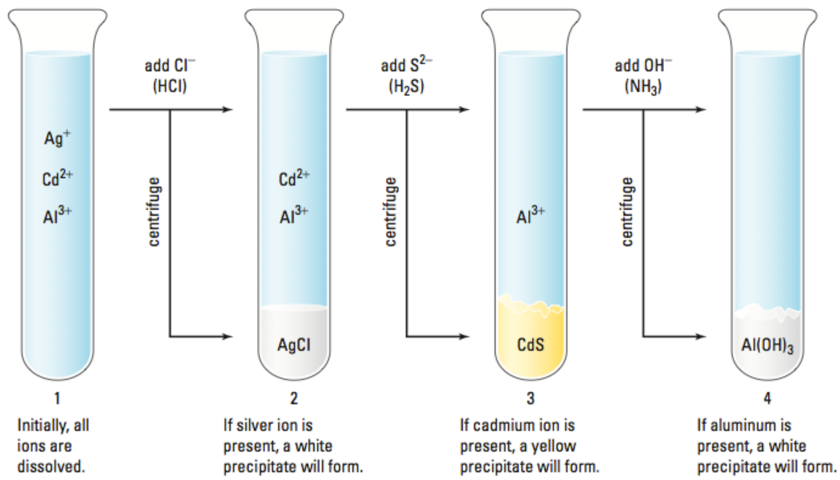
- Process that selectively precipitates ions from solution
- Ex: Cl^-, Br^- and I^-

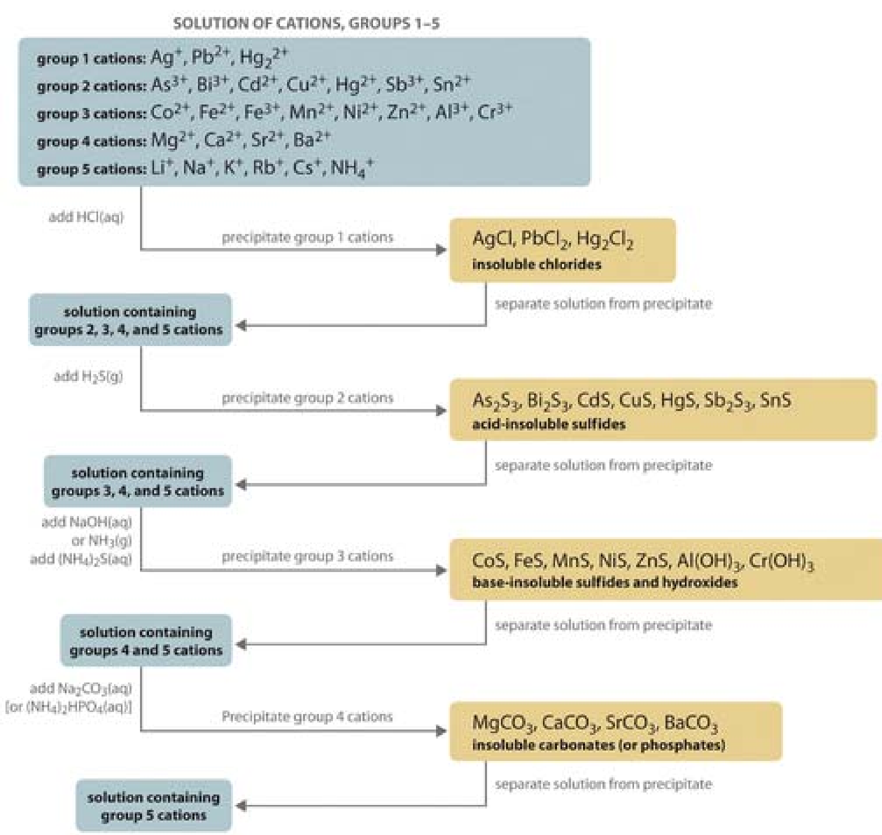
Silver halide	K_{sp}
AgCl	1.8×10^{-10}
AgBr	3.3×10^{-13}
AgI	1.5×10^{-16}

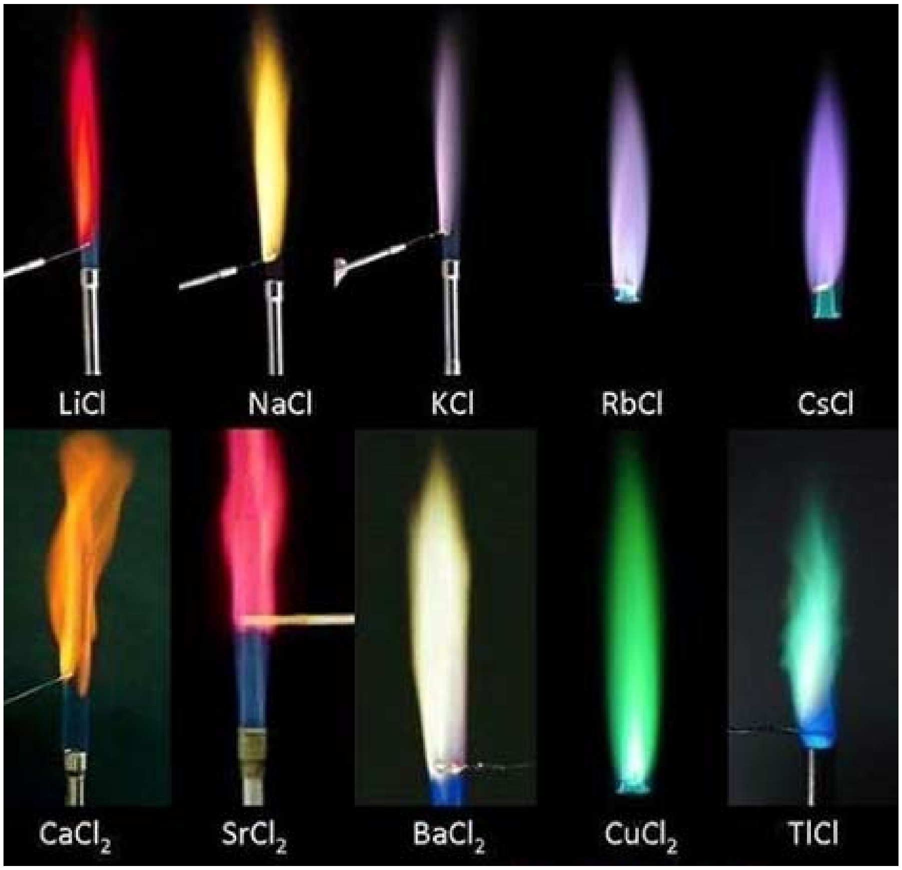
- To separate the halide ions, silver ions are added until most of the AgI is precipitated out
- AgI is removed by filtration or a centrifuge
- Repeat the process with AgBr
- Final solution will only contain Cl^-

Qualitative Analysis

- An older technique since chemists use spectrophotometers
- Ex: Ag^+, Cd^{2+} and Al^{3+}







Checkpoint

Consider a solution that contains Pb^{2+}, Cu^{2+}, and Mg^{2+} cations, present as their (soluble) nitrate salts. How could you selectively precipitate these cations, given solutions of NaCl, Na_2S, and Na_3PO_4?