CHEMISTRY 203

Semi-micro Qualitative Analysis of Ag^{+}, Cu^{2+}, Fe^{2+} and Al^{3+}

Purpose:

- To ***separate*** and ***identify*** silver ion (Ag^{+}), copper ion (Cu^{++}), ferric ion (Fe^{3+}) and aluminum ion (Al^{3+}) when present in a mixture.

- To ***identify*** the ions present in an ***unknown*** mixture.

Qualitative Analysis

Qualitative analysis is concerned with the ***separation*** and ***identification*** of various constituents in the mixture. It is a method for the determination of the types of ions present in a solution.

- Analysis is carried out ***systematically.***
- Separation of ions into groups is made as ***selective*** as possible by adding a specific ***group reagent.***
- Separation of cations at each step must be carried out as ***completely*** as possible.
- Separation is based on selective ***precipitation, amphoterism,*** or ***complexation*** methods.

Group Reagent is the reagent that, when added to a mixture of ions, precipitate one or more ions and leave the others in solution

Separation based on Precipitation

Consider an aqueous solution, which contains salts of all the following ions:

Ag^+, Hg_2^{2+}, Pb^{2+}, Hg^{2+}, Cu^{2+}, Fe^{3+}, Al^{3+}, Mg^{2+}, Ca^{2+}, K^+, Na^+, and NH_4^+

The above cations can be separated into ***five*** groups

Group	Group reagent	Cations precipitated
I	HCl (Cl^-)	Ag^+, Pb^{2+}, Hg_2^{2+}
II	H_2S in acid (S^{2-})	Pb^{2+}*, Hg^{2+}, Cu^{2+}
III	NH_3 + NH_4Cl (OH^-)	Al^{3+}, Fe^{3+}
IV	No common reagent	Ca^{2+} , as $CaCO_3$, Mg^{2+} as $MgNH_4PO_4$
V	No precipitating Reagent	***Soluble ions*** ***Na^+, K^+, NH_4^+***

Group V the "***soluble***" ions Na^+, K^+, NH_4^+ are determined by tests other than those involving precipitation.

*$PbCl_2$ is relatively soluble (K_{sp}= 2.4 x 10^{-4}) and consequently not all Pb^{2+} is precipitated in Group I.

Note that the separation of ions depends on the concentration of the reactants. In order for precipitation to occur, the ion product must exceed $\mathbf{K_{sp}}$.

Solubility Product: K_{sp}

Consider a saturated solution of AgCl that is in contact with solid AgCl.

The solubility equilibrium can be represented as

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

$$K_{sp} = [Ag^+][Cl^-] = 1.6 \times 10^{-10}$$

Solubility product of a compound is the product of the ***molar*** concentration of constituent ions each raised to the ***power*** of its ***stoichiometric coefficient*** in the equilibrium expression.

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

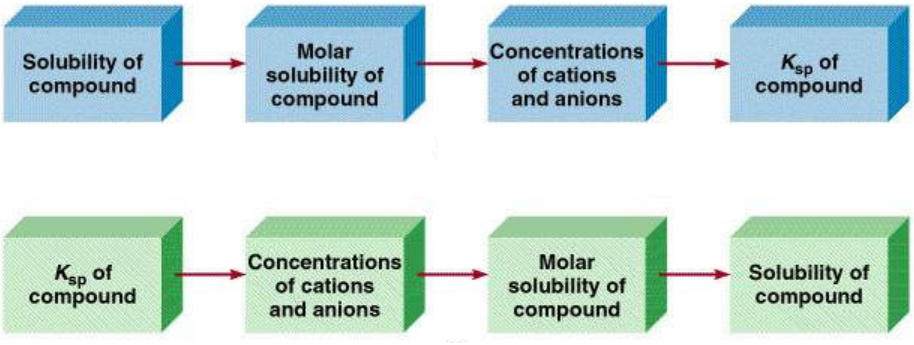
$$K_{sp} = [Pb^{2+}][Cl^-]^2 = 2.4 \times 10^{-4}$$

- The value of K_{sp} indicates the ***solubility*** of an ionic compound.
- The ***smaller*** the value of K_{sp}, the ***less*** soluble the compound.
- In using K_{sp} values to compare solubility, you should chose compounds that have ***similar*** formulas; Otherwise, calculate the solubility of each compound and compare them.

Compound	K_{sp}
AgCl	1.6×10^{-10}
AgBr	7.7×10^{-13}
AgI	8.3×10^{-17}

Molar solubility (***mol/L***) is the number of ***moles*** of solute dissolved in 1 L of a saturated solution.

Solubility (***g/L***) is the number of ***grams*** of solute dissolved in 1 L of a saturated solution.



K_{sp} & Molar Solubility

TABLE 16.3 Relationship between K_{sp} and Molar Solubility (s)

Compound	K_{sp} Expression	Cation	Anion	Relation between K_{sp} and s
AgCl	$[Ag^+][Cl^-]$	s	s	$K_{sp} = s^2;\ s = (K_{sp})^{\frac{1}{2}}$
$BaSO_4$	$[Ba^{2+}][SO_4^{2-}]$	s	s	$K_{sp} = s^2;\ s = (K_{sp})^{\frac{1}{2}}$
Ag_2CO_3	$[Ag^+]^2[CO_3^{2-}]$	$2s$	s	$K_{sp} = 4s^3;\ s = \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}$
PbF_2	$[Pb^{2+}][F^-]^2$	s	$2s$	$K_{sp} = 4s^3;\ s = \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}$
$Al(OH)_3$	$[Al^{3+}][OH^-]^3$	s	$3s$	$K_{sp} = 27s^4;\ s = \left(\frac{K_{sp}}{27}\right)^{\frac{1}{4}}$
$Ca_3(PO_4)_2$	$[Ca^{2+}]^3[PO_4^{3-}]^2$	$3s$	$2s$	$K_{sp} = 108s^5;\ s = \left(\frac{K_{sp}}{108}\right)^{\frac{1}{5}}$

- Solubility product K_{sp} is an equilibrium constant.
- Molar solubility, solubility and solubility product all refer to a **saturated** solution

What is the solubility of silver chloride in g/L ?

	$AgCl\ (s) \rightleftharpoons$	$Ag^+\ (aq)$	+ $Cl^-\ (aq)$
Initial (M)		0.00	0.00
Change (M)		$+s$	$+s$
Equilibrium (M)		s	s

$K_{sp} = 1.6 \times 10^{-10}$

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

$K_{sp} = s^2$

$s = \sqrt{K_{sp}}$

$s = 1.3 \times 10^{-5}$

$[Ag^+] = 1.3 \times 10^{-5}\ M \quad [Cl^-] = 1.3 \times 10^{-5}\ M$

Solubility of AgCl =

$$\frac{1.3 \times 10^{-5}\ \text{mol AgCl}}{1\ \text{L soln}} \times \frac{143.35\ \text{g AgCl}}{1\ \text{mol AgCl}} = 1.9 \times 10^{-3}\ \text{g/L}$$

If 2.00 mL of 0.200 *M* NaOH are added to 1.00 L of 0.100 *M* $CaCl_2$, will a precipitate form?

The ions present in solution are Na^+, OH^-, Ca^{2+}, Cl^-.

Only possible precipitate is $Ca(OH)_2$ (solubility rules).

Is $Q > K_{sp}$ for $Ca(OH)_2$?

Initial concentrations of the ions = $\dfrac{\#\text{ of moles of ion}}{\text{total volume (L)}}$

$[Ca^{2+}]_0 = 0.100\ M$ $\quad [OH^-]_0 = 4.00 \times 10^{-4}\ M$

$Q = [Ca^{2+}]_0[OH^-]_0^2 = 0.100 \times (4.00 \times 10^{-4})^2 = 1.60 \times 10^{-8}$

$K_{sp} = [Ca^{2+}][OH^-]^2 = 8.0 \times 10^{-6}$

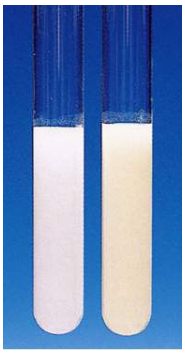
$Q < K_{sp}$ $\quad$ ***No*** precipitate will form

What concentration of Ag is required to precipitate ONLY AgBr in a solution that contains both Br^- and Cl^- at a concentration of 0.02 *M*?

$AgBr\ (s) \rightleftharpoons Ag^+\ (aq) + Br^-\ (aq)$ $\quad K_{sp} = 7.7 \times 10^{-13}$

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

$$[Ag^+] = \frac{K_{sp}}{[Br^-]} = \frac{7.7 \times 10^{-13}}{0.020} = 3.9 \times 10^{-11}\ M$$



$AgCl\ (s) \rightleftharpoons Ag^+\ (aq) + Cl^-\ (aq)$ $\quad K_{sp} = 1.6 \times 10^{-10}$

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

$$[Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{1.6 \times 10^{-10}}{0.020} = 8.0 \times 10^{-9}\ M$$

$3.9 \times 10^{-11}\ M < [Ag^+] < 8.0 \times 10^{-9}\ M$

The Common Ion Effect and Solubility:

The ***common ion effect*** is the shift in equilibrium caused by the addition of a compound having an ion in common with the dissolved substance.

The presence of a common ion **decreases** the solubility of the salt.

What is the molar solubility of AgBr in (a) pure water and (b) 0.0010 *M* NaBr?

$AgBr\ (s) \rightleftharpoons Ag^+\ (aq) + Br^-\ (aq)$

$K_{sp} = 7.7 \times 10^{-13}$

$s^2 = K_{sp}$

$s = 8.8 \times 10^{-7}$

$NaBr\ (s) \longrightarrow Na^+\ (aq) + Br^-\ (aq)$

$[Br^-] = 0.0010\ M$

$AgBr\ (s) \rightleftharpoons Ag^+\ (aq) + Br^-\ (aq)$

$[Ag^+] = s$

$[Br^-] = 0.0010 + s \approx 0.0010$

$K_{sp} = 0.0010 \times s$

$s = 7.7 \times 10^{-10}$

Ref. Chang, sect.16.8

Separation based on the amphoterism of certain metal hydroxides:

- Some metal hydroxides will redissolve in an excess of hydroxide ion to yield hydroxy-complex ions.
- In such a case the slightly soluble metal hydroxide acts as a weak acid toward the base OH^-.
- It is therefore possible to separate amphoteric metal hydroxides from other insoluble hydroxides.
- After filtration, the complex ion in the filtrate may be destroyed by addition of acid to yield the sample metal ion.

$Al^{3+}\ (aq) + 3\ OH^-\ (aq) \rightleftharpoons Al(OH)_3\ (s)$

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

$Al(OH)_4^-\ (aq) + 4\ H^+\ (aq) \rightleftharpoons Al^{3+}\ (aq) + 4\ H_2O\ (l)$

Separation based on the formation of ammine complexes:

- Certain metal ions complex with ammonia to give ammine complex ions.
- Addition of concentrated ammonia to a mixture of metal ions results in the formation of slightly soluble metal hydroxides (NH_3 reacts as base) followed by complexing of some metal ions (NH_3 reacts as a complexing agent).

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

Flow Diagram

Procedure

- Refer to the Lab. manual for detailed "procedure" and "helpful notes".
- Do the analysis for a known solution (containing the four cations).
- Obtain from your instructor an unknown solution and repeat the same procedure to find what cations it contains.
- Write the equations of all chemical reactions involved in this experiment.