Nuclear Process & Radio-Analytical Chemistry

Class Notes – Section 2.3

Separation Chemistry Fundamental (III)

Chung-King Liu

Separation Chemistry Fundamental

- Introduction
- Oxidation/Reduction Processes
- Common Oxidation States
- Common Oxidizing and Reducing Agents
- Nomenclature of selected inorganic compounds
- Precipitation (insoluble salts)
- Solvent Extraction
- Ion-Exchange Chromatography
- Complexation
- Generalized chemical procedure for Actinide elements

Nuclear Process Chemistry Lesson 3

- Nomenclature of selected inorganic compounds
- Precipitation (insoluble salts)
- Solvent Extraction
- Ion-Exchange Chromatography

Nomenclature of selected inorganic compounds

- Names of compounds are usually derived from the names of the elements in the compound.
- Compounds containing a metal will be based on the name of the elemental metal plus the name of the anion.
- The name of simple nonmetal anions convert the ending of the element name with -ide. Polyatomic anions usually end with -ite or -ate. (Note that hydroxide, OH-, is an exception.)

Nomenclature of selected inorganic compounds

common anions containing nonmetals

symbol	name	symbol	name	symbol	name	symbol	name
F^-	fluoride						
Cl^-	chloride	ClO_2^-	chlorite	ClO_3^{2-}	chlorate	ClO_4^-	perchlorate
Br^-	bromide			BrO_3^{2-}	bromate		
I^-	iodide			IO_3^{2-}	iodate		
O^{2-}	oxide	OH^-	hydroxide			O_2^{2-}	peroxide
S^{2-}	sulfide	SO_3^{2-}	sulfite	SO_4^{2-}	sulfate		
Se^{2-}	selenide						
N^{3-}	nitride	NO_2^-	nitrite	NO_3^-	nitrate		
P^{3-}	phosphide			PO_4^{3-}	phosphate		
As^{3-}	arsenide			AsO_3^{2-}	arsenate		
C^{4-}	carbide			CO_3^{2-}	carbonate		
Si^{4-}	silicide			SiO_4^{4-}	silicate		

Nomenclature of selected inorganic compounds

Common organic anions

CH_3COO^{-1}	acetate
$HCOO^{-1}$	formate
$C_2O_4^{-2}$	oxalate

Nomenclature of selected inorganic compounds

Common anions containing metals

MnO_4^{-1}	permanganate
CrO_4^{-2}	chromate
$Cr_2O_7^{-2}$	dichromate

Nomenclature of selected inorganic compounds

Metals with multiple oxidation states use a Roman numeral in parentheses to specify the oxidation state. Examples:

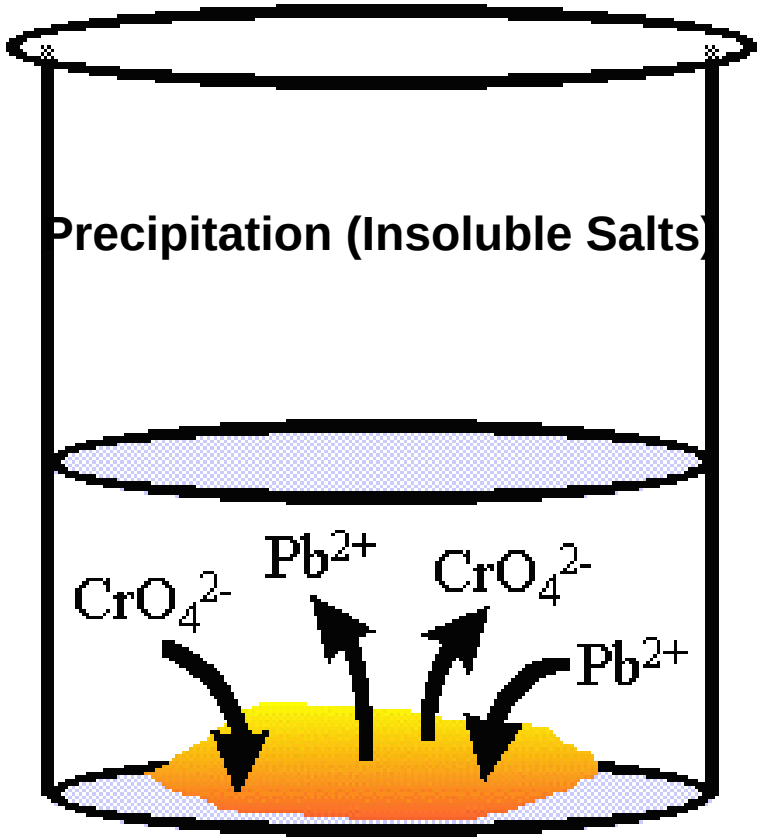
Formula	Write as	Read as
FeCl	Iron(II) chloride	Iron two chloride
FeCl	Iron(III) chloride	Iron three chloride

Nomenclature of selected inorganic compounds

Nonmetals

Formula	Read as
CO	Carbon monoxide
CO_2	Carbon dioxide
SO2	Sulfur dioxide
SO_3	Sulfur trioxide
N_2O_5	Dinitrogen pentoxide

Precipitation (insoluble salts)



(2.3)

Precipitation (insoluble salts)

- Many metal ions form compounds that are insoluble in water. We call them insoluble salts or precipitates.
- Common precipitates are carbonates, hydroxides, sulfates, and phosphates.
-

Precipitation (insoluble salts)

- An insoluble salt in contact with water maintains an equilibrium with the ions.
- In simple cases where there are no common ions or competing equilibria, the ion concentrations depend only on the equilibrium constant for the particular precipitate.

Precipitation (insoluble salts)

When we talk about solubility equilibria we always write the equilibrium with the solid on the left. For example:

$$Ba(IO_3)_2 \rightleftarrows Ba^{+2}_{(aq)} + 2\ IO_3^{-1}{}_{(aq)}$$

Precipitation (insoluble salts)

The equilibrium constant expression for an insoluble salt is written following the same rules as for any other equilibrium. The equilibrium constant is called the solubility product, K_{sp}. The K_{sp} expression for the above equilibrium is:

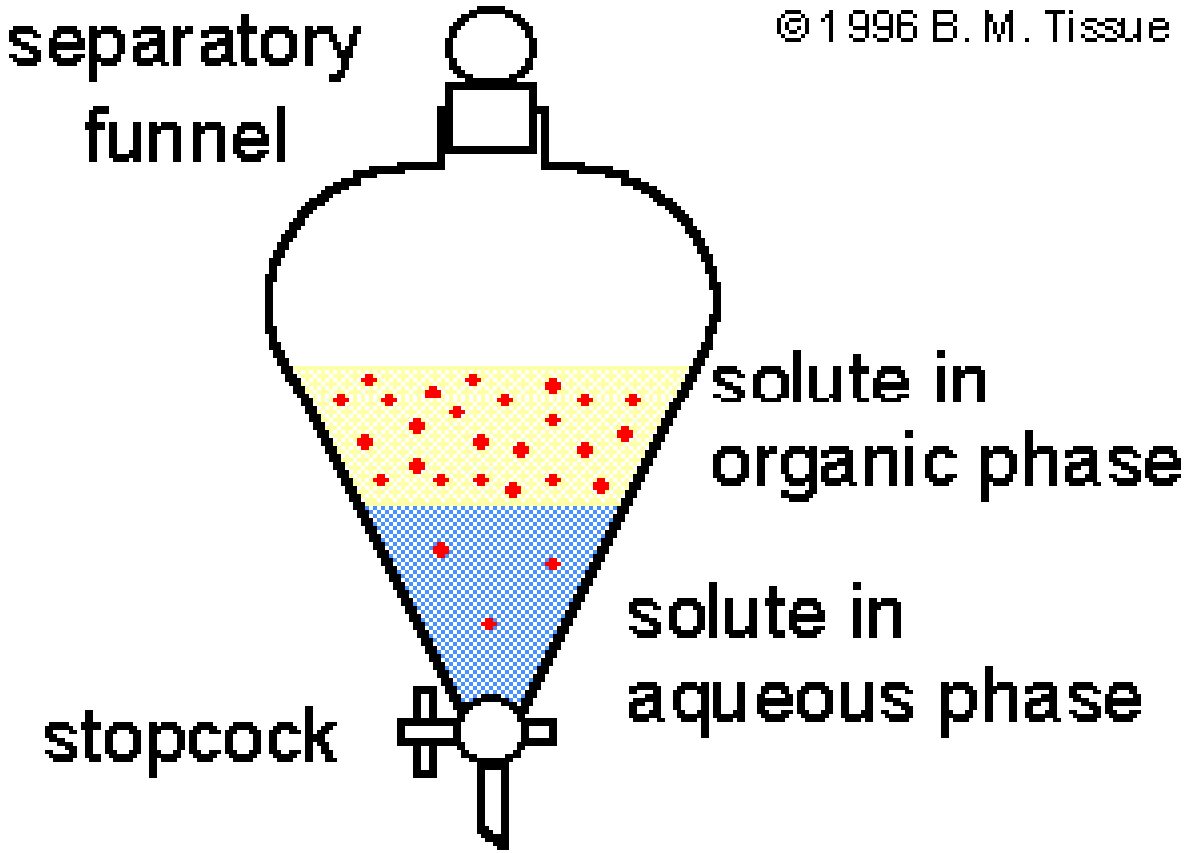
$$K_{sp} = [Ba^{2+}][IO^{3-}]_2$$

Precipitation (insoluble salts)

$K_{sp} = [Ba^{2+}][IO_3^-]^2$

K_{sp} Values for Some Precipitates		
Formula	**Name**	**K_{sp}**
AgCl	silver chloride	1.8×10^{-10}
$Al(OH)_3$	aluminum hydroxide	2×10^{-32}
$BaCO_3$	barium carbonate	5×10^{-9}
$Ba(IO_3)_2$	barium iodate	1.6×10^{-9}
$BaSO_4$	barium sulfate	1.3×10^{-10}
$Fe(OH)_2$	iron(II) hydroxide	8×10^{-16}
$Fe(OH)_3$	iron(III) hydroxide	4×10^{-38}
FeS	iron sulfide	6×10^{-18}
$PbCrO_4$	lead chromate	1.8×10^{-14}
$Pb(OH)_2$	lead hydroxide	2.5×10^{-16}
PbS	lead sulfide	7×10^{-28}
$PbSO_4$	lead sulfate	1.6×10^{-8}

Solvent Extraction



Solvent Extraction

- Solvent extraction refers to the process of selectively removing a solute from a liquid mixture with a solvent
- As a separation technique, it is a partitioning process based on the unequal distribution of solute between two immiscible solvents, usually water (aq) and an organic liquid (org)

Solvent Extraction

- The different solubilities of a solute in the solvent pairs of an extraction system are described by the distribution or partition coefficient, K_d
- K_d is expressed mathematically by:

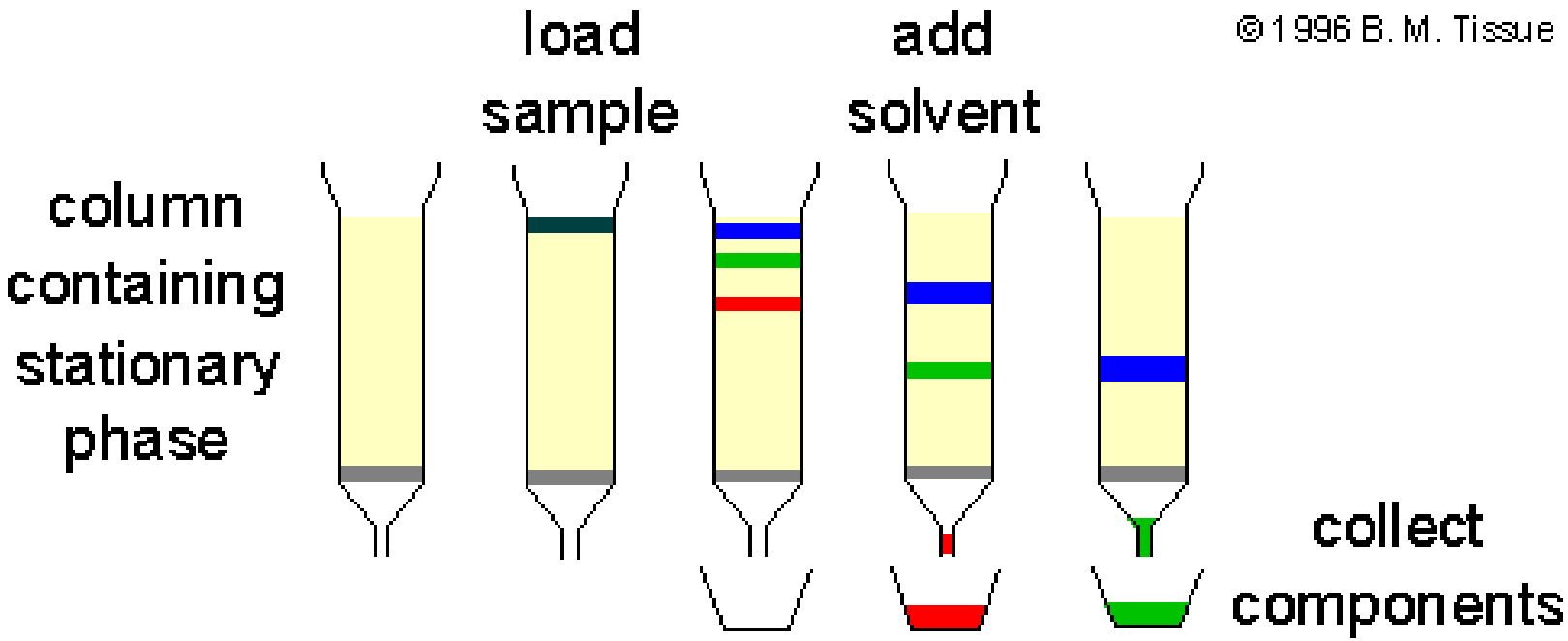
$$K_d = [A_{org}] / [A_{aq}]$$

Solvent Extraction

EFFECT OF NITRIC ACID ON DISTRIBUTION COEFFICIENTS for URANIUM AND PLUTONIUM (in 20% TBP in hydrocarbon)

	Distribution Coefficient	
Metal or Radical	1 M HNO3	6 M HNO3
UO_2^{++}	5	30
PuO_2^{++}	0.7	3
Pu^{4+}	1.3	20
Pu^{3+}	0.015	0.01

Chromatography (IX)



Chromatography (IX)

- IX methods are based on the reversible exchange of metal ions between a liquid phase, typically water, and a solid ionic phase of opposite charge, the resin.
- The resin competes with ion-solvent interactions in the liquid phase, primarily ion-dipole interactions.
- The solid phase consistes of an insoluble, but permeable, inert polymeric matrix that contains fixed charged groups (exchange site or function group) associated with mobile counter-ions of opposite charge.

Chromatography (IX)

In a practical description of ion-exchange equilibria, the weight distribution coefficient, K_d, and the separation factor, ✞, are significant.

$$K_d = (C_1/g_{resin}) / (C_2/mL_{solution})$$

$$\text{Separation factor } (✞) = K_{d,a} / K_{d,b}$$