



# Nuclear Process & Radio-Analytical Chemistry

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Class Notes – Section 2.2

Separation Chemistry Fundamental (II)

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# Separation Chemistry

## Fundamental

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- 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

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



# Nomenclature of selected inorganic compounds

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- 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,  $\text{OH}^-$ , is an exception.)

# Nomenclature of selected inorganic compounds

common anions containing nonmetals							
symbol	name	symbol	name	symbol	name	symbol	name
F <sup>-</sup>	fluoride						
Cl <sup>-</sup>	chloride	ClO <sub>2</sub> <sup>-</sup>	chlorite	ClO <sub>3</sub> <sup>2-</sup>	chlorate	ClO <sub>4</sub> <sup>-</sup>	perchlorate
Br <sup>-</sup>	bromide			BrO <sub>3</sub> <sup>2-</sup>	bromate		
I <sup>-</sup>	iodide			IO <sub>3</sub> <sup>2-</sup>	iodate		
O <sup>2-</sup>	oxide	OH <sup>-</sup>	hydroxide			O <sub>2</sub> <sup>2-</sup>	peroxide
S <sup>2-</sup>	sulfide	SO <sub>3</sub> <sup>2-</sup>	sulfite	SO <sub>4</sub> <sup>2-</sup>	sulfate		
Se <sup>2-</sup>	selenide						
N <sup>3-</sup>	nitride	NO <sub>2</sub> <sup>-</sup>	nitrite	NO <sub>3</sub> <sup>-</sup>	nitrate		
P <sup>3-</sup>	phosphide			PO <sub>4</sub> <sup>3-</sup>	phosphate		
As <sup>3-</sup>	arsenide			AsO <sub>3</sub> <sup>2-</sup>	arsenate		
C <sup>4-</sup>	carbide			CO <sub>3</sub> <sup>2-</sup>	carbonate		
Si <sup>4-</sup>	silicide			SiO <sub>4</sub> <sup>4-</sup>	silicate		

# Nomenclature of selected inorganic compounds

Common organic anions

$\text{CH}_3\text{COO}^{-1}$	acetate
$\text{HCOO}^{-1}$	formate
$\text{C}_2\text{O}_4^{-2}$	oxalate



# Nomenclature of selected inorganic compounds

Common anions containing metals

$\text{MnO}_4^{-1}$	permanganate
$\text{CrO}_4^{-2}$	chromate
$\text{Cr}_2\text{O}_7^{-2}$	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 <sub>2</sub>	Iron(II) chloride	Iron two chloride
FeCl <sub>3</sub>	Iron(III) chloride	Iron three chloride

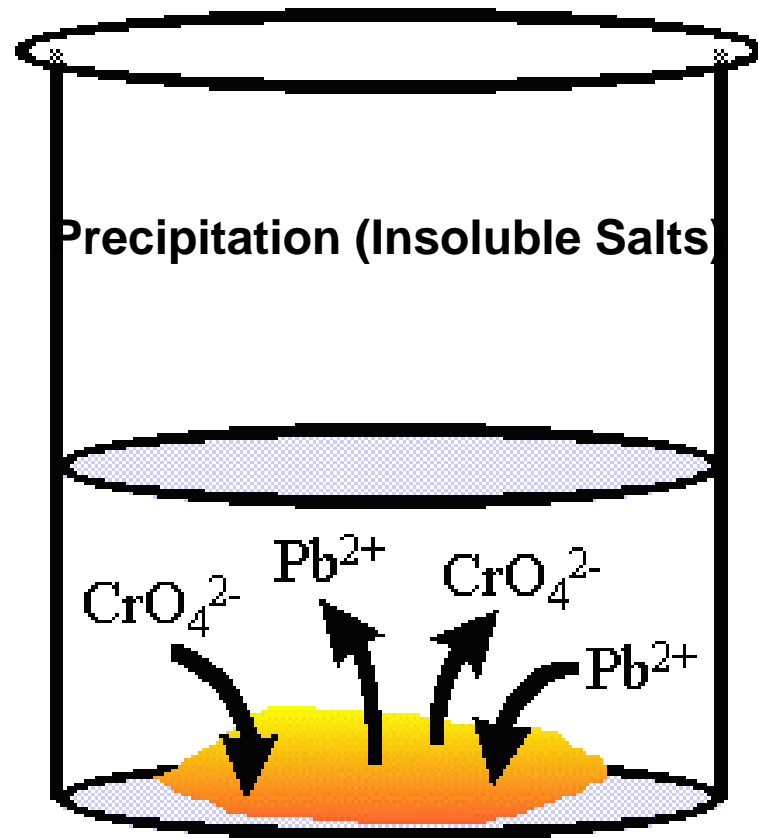


# Nomenclature of selected inorganic compounds

## Nonmetals

Formula	Read as
CO	Carbon monoxide
CO <sub>2</sub>	Carbon dioxide
SO <sub>2</sub>	Sulfur dioxide
SO <sub>3</sub>	Sulfur trioxide
N <sub>2</sub> O <sub>5</sub>	Dinitrogen pentoxide

# Precipitation (insoluble salts)



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# Precipitation (insoluble salts)

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- 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.
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# Precipitation (insoluble salts)

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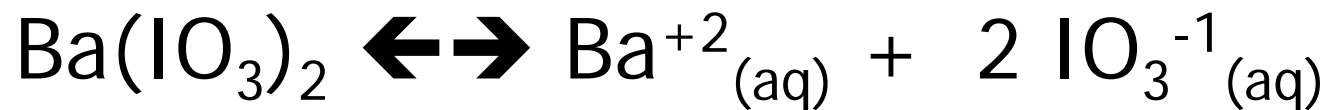
- An insoluble salt in contact with water maintains an equilibrium with the ions.
- In simple cases where there are no common ions or competing equilibria, the ion concentrations depend only on the equilibrium constant for the particular precipitate.



## Precipitation (insoluble salts)

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





# Precipitation (insoluble salts)

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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:

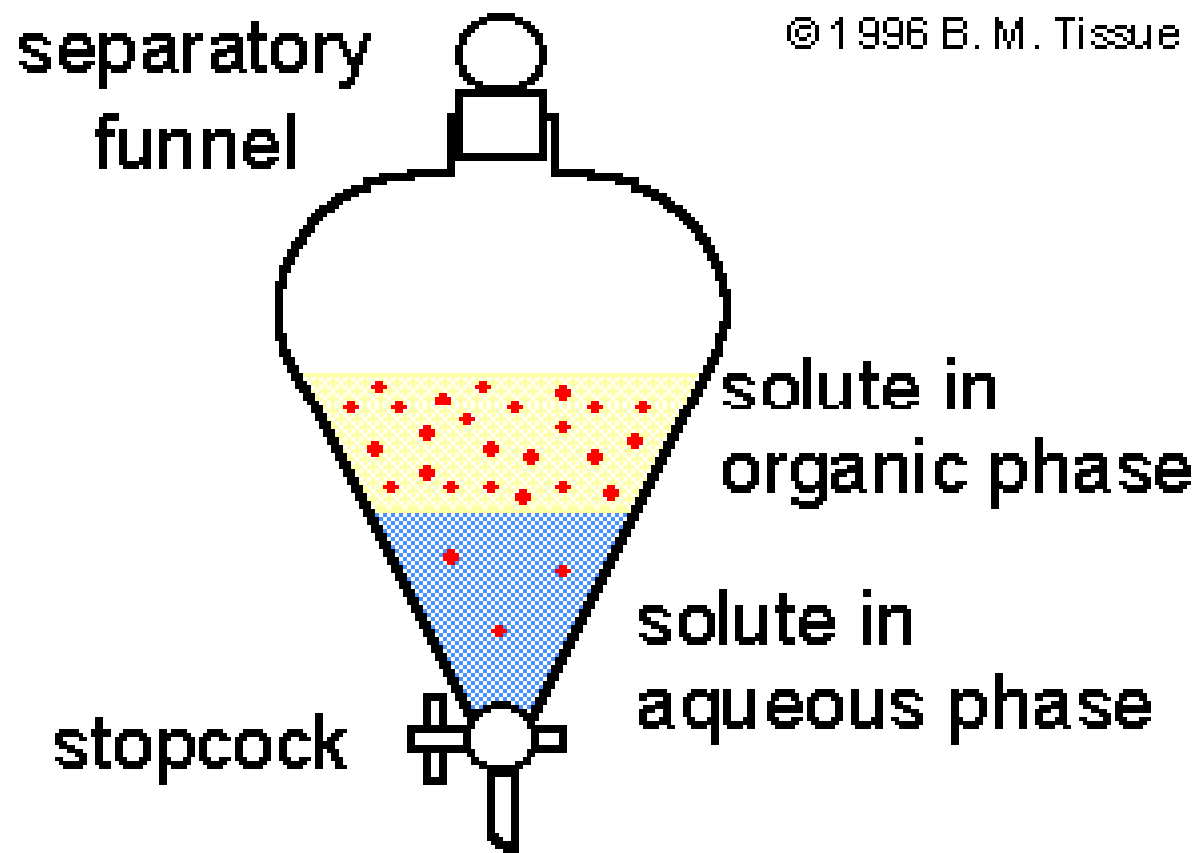
$$K_{sp} = [\text{Ba}^{2+}][\text{IO}_3^-]_2$$

## Precipitation (insoluble salts)

$$K_{sp} = [\text{Ba}^{2+}][\text{IO}_3^-]^2$$

$K_{sp}$ Values for Some Precipitates		
Formula	Name	$K_{sp}$
AgCl	silver chloride	$1.8 \times 10^{-10}$
Al(OH) <sub>3</sub>	aluminum hydroxide	$2 \times 10^{-32}$
BaCO <sub>3</sub>	barium carbonate	$5 \times 10^{-9}$
Ba(IO <sub>3</sub> ) <sub>2</sub>	barium iodate	$1.6 \times 10^{-9}$
BaSO <sub>4</sub>	barium sulfate	$1.3 \times 10^{-10}$
Fe(OH) <sub>2</sub>	iron(II) hydroxide	$8 \times 10^{-16}$
Fe(OH) <sub>3</sub>	iron(III) hydroxide	$4 \times 10^{-38}$
FeS	iron sulfide	$6 \times 10^{-18}$
PbCrO <sub>4</sub>	lead chromate	$1.8 \times 10^{-14}$
Pb(OH) <sub>2</sub>	lead hydroxide	$2.5 \times 10^{-16}$
PbS	lead sulfide	$7 \times 10^{-28}$
PbSO <sub>4</sub>	lead sulfate	$1.6 \times 10^{-8}$

# Solvent Extraction





# Solvent Extraction

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- 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

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- 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:

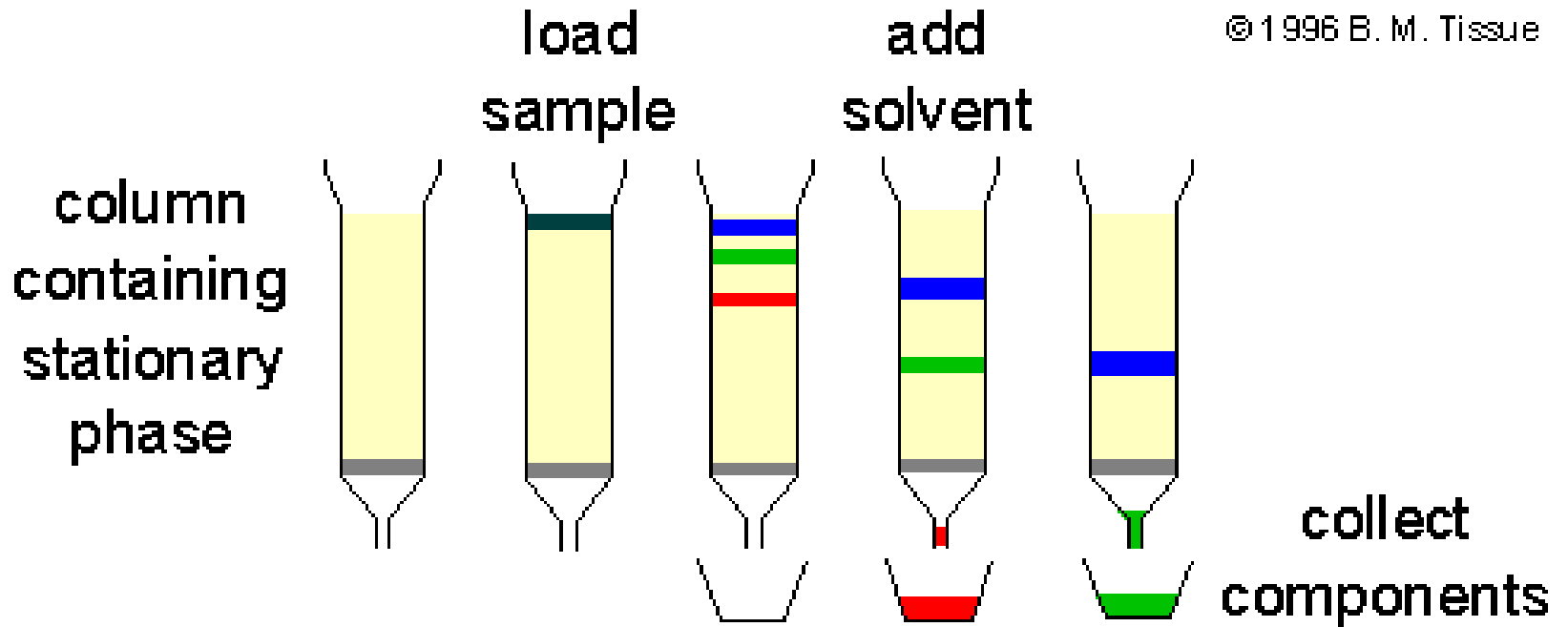
$$K_d = [A_{\text{org}}] / [A_{\text{aq}}]$$

# Solvent Extraction

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

Metal or Radical	Distribution Coefficient	
	1 <u>M</u> HNO <sub>3</sub>	6 <u>M</u> HNO <sub>3</sub>
UO <sub>2</sub> ++	5	30
PuO <sub>2</sub> ++	0.7	3
Pu 4+	1.3	20
Pu 3+	0.015	0.01

# Chromatography (IX)





# Chromatography (IX)

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- 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 consists 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)

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

$$K_d = (C_1/g_{\text{resin}}) / (C_2/\text{mL}_{\text{solution}})$$

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