



# Nuclear Process & Radio-Analytical Chemistry

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Class Notes – Section 2.1

Separation Chemistry Fundamental (I)

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# Separation Chemistry Fundamental

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- Introduction
- Oxidation/Reduction Processes
- Common Oxidation States
- Common Oxidizing and Reducing Agents
- Complexation
- Solvent Extraction
- Ion-Exchange Chromatography
- Precipitation and Co-precipitation
- Generalized chemical procedure for Actinide elements



# Review of Lecture 1

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- Same oxidation number = similar separation chemistry



# Review of Lecture 1

## Solubility rules

	$\text{NO}_3^{-1}$	$\text{F}^{-1}$	$\text{OH}^{-1}$	$\text{SO}_4^{-2}$	$\text{PO}_4^{-3}$	$\text{CO}_3^{-2}$
$\text{M}^{+1}$	S	S	S	S	S	S
$\text{M}^{+2}$	S	I	I*	I*	I	I
$\text{M}^{+3}$	S	I	I	I	I	I
$\text{M}^{+4}$	S	I	I	I	I	I
$\text{M}^{+5}$	S	S	S	S	S	S
$\text{M}^{+6}$	S	S	S	S	S	S

S: Soluble in water

I: Insoluble in water

I\* Insoluble in water for most compounds with few exceptions



# Introduction

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- Review of important chemical principles that constitute the foundation of separation chemistry
- Purposely selected an EPA radiochemical procedure to provide illustrations for separation chemistry principles
- Carrier and co-precipitation



# Oxidation/Reduction (redox) Chemistry

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- Redox play an important role in **dissolution & separation** in nuclear chemical processes
- Oxidation # can affect 1) chemical stability; 2) reactivity with separating material; 3) solubility in the presence of other ions; 4) behavior in the presence of carriers



# Oxidation/Reduction (redox) Chemistry

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- Differences in mass number of all radionuclides of an element are so small that elements with the same oxidation # will exhibit the same chemical behavior during nuclear chemical process



# Redox Reactions

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- Redox is reaction in which electrons are redistributed among the atoms, molecules, or ions in the reaction
- Oxidation is defined as the loss of electron(s) by a chemical species
- Reduction is defined as the gain of electron(s)



# Redox Reactions

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- $\text{U} + 3 \text{F}_2 \rightarrow \text{U}^{+6} + 6 \text{F}^{-1}$
- $\text{Pu}^{+4} + \text{Fe}^{+2} \rightarrow \text{Pu}^{+3} + \text{Fe}^{+3}$
- $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$



# Redox Reactions

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- At least one species is oxidized and at least one species is reduced simultaneously
- **Oxidizing agent** is defined as the substance that causes oxidation of another species by accepting electron from it or increasing in electron density; it is thereby **reduced itself**
- **Reducing agents** lose electron or electron density and are therefore **oxidized**



# Oxidation Number

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- Oxidation numbers are a relative indication of the electron density associated with an atom of an element
- Numbers change during redox reactions, whether they occur by actual transfer of an electron or by unequal sharing of electrons in a covalent bond



# Assigning oxidation numbers

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- In this set, the rules for assigning oxidation numbers are listed in order by priority of application; that is, the rule written first in the list has priority over the rule below it



# Oxidation Number

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- Sum of oxidation# of all atoms in a chemical species adds up to equal the charge on the species. Zero for elements and compounds
- IA = +1; IIA = +2
- F = -1; H = +1
- O = -2
- VIIA elements = -1
- O, S, Se, Te, Po = -2 (for Binary compounds)



# Assigning oxidation numbers

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- Metallic uranium,  $O_2$ ,  $Cl_2$
- $CO_2$
- $UO_2^{+2}$ ,  $NpO_2^{+1}$ ,  $PuO_2^{+2}$
- $Na_2Cr_2O_7$



# Common Oxidation States

- In 0.5 M HCl at 25 degree C, the equilibrium % of plutonium in the various oxidation states are found to be as follows:

$\text{Pu}^{+3}$	27.2%
$\text{Pu}^{+4}$	58.4%
$\text{Pu}^{+5}$	~0.7%
$\text{Pu}^{+6}$	13.6%



# Common Oxidation States

In  $\text{HNO}_3/\text{HNO}_2$  solution, majority of each actinide will be shown the following oxidation states:

Actinide	Oxidation #
Am	+3
Pu	+4
Np	+5
U	+6



# Oxidation States of Elements

Element	Oxidation #	Chemical Form
Am	+3	$\text{Am}^{+3}$
Fe	+2	$\text{Fe}(\text{H}_2\text{O})_6^{+2}$
	+3	$\text{Fe}(\text{H}_2\text{O})_6^{+3}$
I	-1	$\text{I}^{-1}$
	+5	$\text{IO}_3^{-1}$
	+7	$\text{IO}_4^{-1}$



# Oxidation States of Elements

(continued)

Element	Oxidation #	Chemical Form
Mn	+2	$\text{Mn}^{+2}$
	+4	$\text{Mn}^{+4}$
	+7	$\text{MnO}_4^{-1}$
Tc	+4	$\text{TcO}_3^{-2}$
	+7	$\text{TcO}_4^{-1}$
Th	+4	$\text{Th}(\text{H}_2\text{O})_8^{+4}$

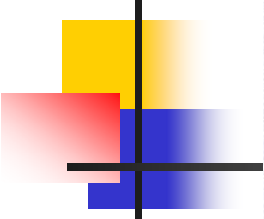


# Oxidation States of Elements

(continued)

Element	Oxidation #	Chemical Form
U, Pu, or Np	+3	$\text{Pu}(\text{H}_2\text{O})_x^{+3}$
	+4	$\text{Pu}(\text{H}_2\text{O})_x^{+4}$
	+5	$\text{PuO}_2^{+1}$
	+6	$\text{PuO}_2^{+2}$
Zr	+4	$\text{Zr}(\text{H}_2\text{O})_{6,8,16}^{+4}$

# Stable oxidation states of selected elements



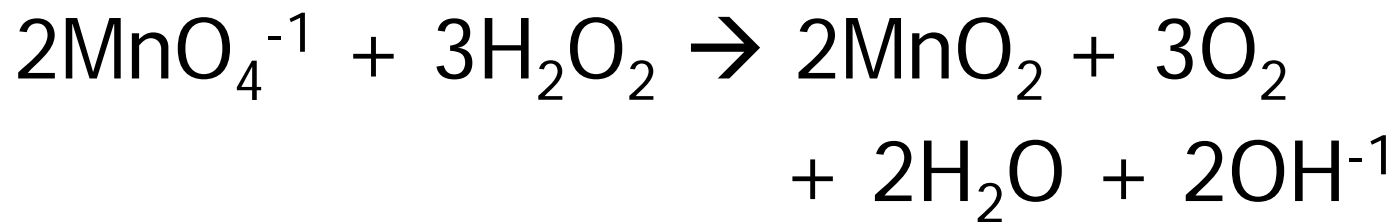
Element	+1	+2	+3	+4	+5	+6	+7	+8
Titanium		○	○	●				
Vanadium		○	○	●	●			
Chromium		●	●	○	○	●		
Manganese		●	○	●	○	○	●	
Iron		●	●	○		○		
Cobalt		●	●					
Nickel		●	○	○				
Strontium		●						
Yttrium			●					
Molybdenum		○	○	●	●	●		
Technetium		○	○	●	○	○	●	
Silver	●		○	○				
Cesium	●							
Barium		●						
Lanthanides			●					
Lead		●		○				
Polonium		○		●		○		
Radium		●						
Actinium			●					
Thorium				●				
Protactinium				○	●			
Uranium			○	○	○	●		
Neptunium			○	○	●	○	○	
Plutonium			○	●	○	○		
Americium			●	○	○	○		
Curium			●	○				

# Common Oxidizing & Reducing Agents

- Hydrogen peroxide serve as an oxidizing agent:



- Serve as a reducing agent:





# Redox reagents for used in nuclear process industry

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Strong oxidizing agents

( $\text{Pu}^{+3}/\text{Pu}^{+4} \rightarrow \text{Pu}^{+6}$ ):

- 1)  $\text{K}_2\text{Cr}_2\text{O}_7$
- 2)  $\text{KMnO}_4$
- 3)  $\text{Ag}^{+2}$
- 4)  $\text{NaBiO}_3$  (Sodium Bismuthate)
- 5)  $\text{Ce}^{+4}$



# Redox reagents for used in nuclear process industry

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Strong reducing agents ( $\text{Pu}^{+4} \rightarrow \text{Pu}^{+3}$ ):

- 1) Zn metal
- 2)  $\text{Fe}^{+2}$
- 3) NaI ( $\text{I}^{-1}$ )
- 4)  $\text{NH}_2\text{OH} \cdot \text{HNO}_3$  (hydroxylamine nitrate)
- 5)  $\text{Ti}^{+3}$  &  $\text{U}^{+4}$