

# **CHAPTER 16:**

## **Redox Titrations**

**(Note: Review Chapters 7&11)**

# **I. Reagents for Redox Titration**

## **➤ Preparation of Standard Solutions for**

**a. Oxidizing Reagents**

**b. Reducing Reagents**

## **➤ Standardization of**

**a. Oxidizing Reagents**

**b. Reducing Reagents**

➤ **Selection of Indicators**

**II. Criteria of Primary and Secondary Standards  
(Review Chapters 7&11)**

**III. Calculation of concentrations  
(Review Chapters 7&11)**

$$C_x = \frac{\text{Number of Moles of } x \text{ (mole)}}{\text{Volume of Solution (L)}}$$

$$\text{Number of Moles of } x = \frac{\text{Weight of } x}{\text{MW of } x}$$

## IV. Examples of Standards

➤ **Standards for standardization of reducing agents:**

- $\text{K}_2\text{Cr}_2\text{O}_7$
- $\text{KIO}_3$
- $\text{Ce}^{4+}$

➤ **Standards for standardization of oxidizing agents:**

- $\text{Na}_2\text{C}_2\text{O}_4$
- $\text{Na}_2\text{S}_2\text{O}_3$
- $\text{Fe}^{2+}$  (Mohr's salt and Oesper's salt)

## **V. Auxiliary Oxidizing and Reducing Agents**

- **The analyte must be in a single oxidation state at the start of the titration.**
- **This can be achieved by using a pre-oxidation or pre-reduction step prior to analysis**

## **A. Auxiliary Reducing Agents:**

- **Metals are one group of reducing agents often used.**
- **The metal (Ni, Zn, Al, Cd, Pb, etc) may be used depending on the reduction potential of the metal relative to that of the analyte).**
- **The metal may be mixed directly with analyte solution and removed mechanically or by filtration.**

- **Jones Reductor:** 2 cm column packed with amalgamated Zn (the amalgam inhibits formation of  $H_2$  from any  $H^+$  which may be necessary in the analyte solution).
- **Walden Reductor:** granular Ag in a narrow glass column. Requires the presence of anion which forms insoluble silver salt (using HCl solutions for analyte)

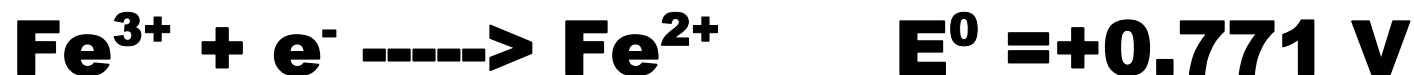
## **B. Auxiliary Oxidizing Agents:**

- **NaBiO<sub>3</sub> (sodium bismuthate) can convert Mn<sup>2+</sup> to MnO<sub>4</sub><sup>-</sup>.**
- **(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (ammonium peroxydisulfate) can convert Cr<sup>3+</sup> to Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, Ce<sup>3+</sup> to Ce<sup>4+</sup>, and Mn<sup>2+</sup> to MnO<sub>4</sub><sup>-</sup>.**
- **H<sub>2</sub>O<sub>2</sub> (Hydrogen peroxide)**

## **VI. Applications of Standard Reductants:**

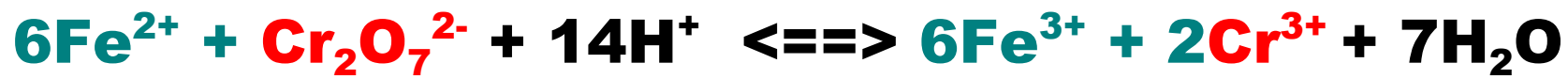
### **A. Iron(II) solutions: prepared from**

- **$\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (Mohr's salt) or**
- **$\text{Fe}(\text{C}_2\text{H}_4)(\text{NH}_3)_2(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  (Oseper's salt)**



- **Applications of  $\text{Fe}^{2+}$ : determination of**
  - **$\text{Cr}_2\text{O}_7^{2-}$**
  - **$\text{Ce}^{4+}$**
  - **$\text{ClO}_3^-$**
  - **Organic peroxides, other oxidants**

**Example 1:** A solution prepared by dissolving a 0.2464-g sample of electrolytic iron wire in acid was passed through a Jones reactor. The iron(II) in the resulting solution required a 39.31-mL titration. Calculate the molar oxidant concentration if the titrant used was (b)  $\text{Cr}_2\text{O}_7^{2-}$  (product  $\text{Cr}^{3+}$ ).



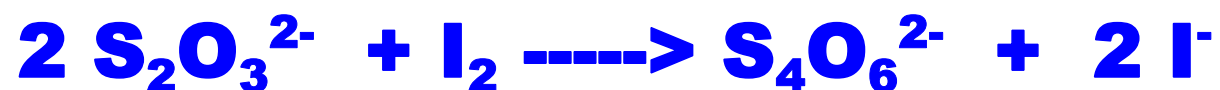
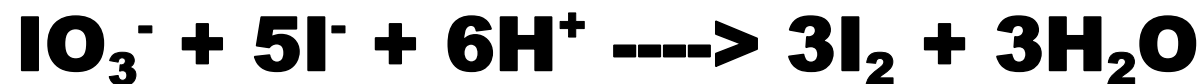
$$\frac{\text{moles of Fe}^{2+}}{\text{moles of Cr}_2\text{O}_7^{2-}} = \frac{\frac{W_{\text{Fe}}}{\text{MW of Fe}}}{C_{\text{Cr}_2\text{O}_7^{2-}} V_{\text{Cr}_2\text{O}_7^{2-}}} = \frac{6}{1}$$

$$C_{\text{Cr}_2\text{O}_7^{2-}} = 0.01871 \text{ M}$$

**B. Sodium Thiosulfate:  $\text{Na}_2\text{S}_2\text{O}_3$**

- **Stability of  $\text{Na}_2\text{S}_2\text{O}_3$** 
  - **Relatively stable in the air, but slowly decompose to  $\text{HSO}_3^-$  and S.**
  - **Sensitive to pH,  $\text{Cu}^{2+}$ , light, bacteria...**
  - **Needed to be re-standardized**
  
- **Standardization of  $\text{Na}_2\text{S}_2\text{O}_3$** 
  - **Primary standard ( $\text{KIO}_3$ )**
  - **Dissolve  $\text{KIO}_3$  in an excess of KI**
  - **Starch as an indicator**
  - **blue starch- $\text{I}_3^-$  is titrated with  $\text{Na}_2\text{S}_2\text{O}_3$  until the blue color disappears (all  $\text{I}_2$  turn to  $\text{I}^-$ ).**

## Reactions:



**Note:** The stoichiometry of reactions

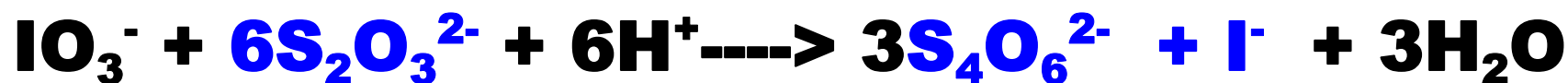
## Example 2:

**Example 2:** A solution of  $\text{Na}_2\text{S}_2\text{O}_3$  was standardized by dissolving 0.1210 g  $\text{KIO}_3$  (MW = 214.00 g/mol) in water,

adding a large excess of KI, and acidifying with HCl. The liberated iodine (I<sub>2</sub>) required 41.64 mL of the Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> to decolorize the blue starch/iodine complex. Calculate the molarity of the Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.



[Eq.1] -[Eq. 2]x3



$$\frac{\text{moles of IO}_3^-}{\text{moles of S}_2\text{O}_3^{2-}} = \frac{\frac{\text{Weight KIO}_3}{\text{MW KIO}_3}}{C_{\text{S}_2\text{O}_3^{2-}} V_{\text{S}_2\text{O}_3^{2-}}} = \frac{1}{6}$$

$$C_{\text{S}_2\text{O}_3^{2-}} = 0.08147 \text{ M}$$

➤ **Applications of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>:**

## determination of

- $\text{IO}_4^{2-}$
- $\text{IO}_3^{2-}$
- $\text{ClO}_3^-$
- $\text{BrO}_3^-$
- $\text{Br}_2$
- $\text{Cl}_2$

## VII. Applications of Standard Oxidants

## The strong oxidants:

### ➤ Applications of $\text{MnO}_4^-$

#### VII-1: $\text{MnO}_4^-$ : at $\text{pH} < 1$



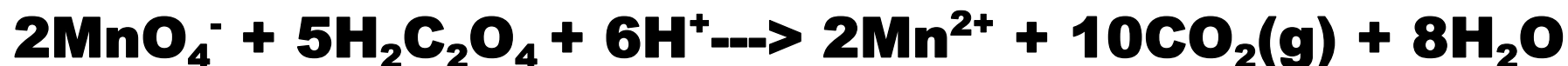
### ➤ Stability of $\text{MnO}_4^-$

- not stable and decompose into  $\text{MnO}_2$
- needed to be filtered and re-standardized
- reactions depend upon pH

### ➤ Standardization of $\text{MnO}_4^-$

- **Primary standard (Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>)**
- **Auto-catalysis by Mn<sup>2+</sup>**
- **In hot and acidity solution**

## Reactions:



## Example 2:

**How to prepare MnO<sub>4</sub><sup>-</sup> solution**

## Examples 3 and 4

$$\frac{\text{moles of C}_2\text{O}_4^{2-}}{\text{moles of MnO}_4^-} = \frac{\text{Weight Na}_2\text{C}_2\text{O}_4}{\text{MW Na}_2\text{C}_2\text{O}_4} = \frac{5}{2}$$

$$C_{\text{MnO}_4^-} V_{\text{MnO}_4^-}$$

**Example 3:** Weight  $\text{Na}_2\text{C}_2\text{O}_4 = 0.101 - 0.151\text{g}$

**Example 4:**  $C_{\text{MnO}_4^-} = 0.01145 \text{ M}$

➤ **Applications of  $\text{Ce}^{4+}$ :**

## VII-2: $\text{Ce}^{4+}$



### ➤ **Stability of $\text{Ce}^{4+}$**

- **Stable in  $\text{H}_2\text{SO}_4$**
- **unstable in  $\text{H}_2\text{NO}_3$  and  $\text{HClO}_3$**
- **can be used as a primary standard**
- **less popular than  $\text{MnO}_4^-$  due to the need of indicator, unstable in  $\text{H}_2\text{NO}_3$  and  $\text{HClO}_3$ , and its cost.**

## VII-3: $\text{Cr}_2\text{O}_7^{2-}$



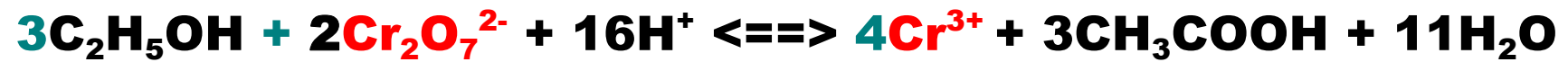
### ➤ **Stability of $\text{Cr}_2\text{O}_7^{2-}$**

- **Stable**
- **can be used as a primary standard**
- **need indicators (Table 16-3)**

### ➤ **Primary applications of $\text{Cr}_2\text{O}_7^{2-}$ :**

- **Determination  $\text{Fe}^{2+}$**
- **Indirect determination of oxidizing agents**
- **Ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) (Example 17-6)**

## **Reactions:**



**VII-4:  $\text{I}_3^-$**



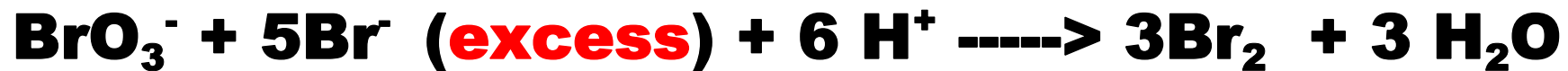
- **Weak oxidizing agents**
- **Unstable**
- **Needed to be re-standardized**
- **Less popular than  $\text{Ce}^{4+}$ ,  $\text{MnO}_4^-$ ,  $\text{Cr}_2\text{O}_7^{2-}$**
- **used for the determination of strong reductants (Table 17-6)**

## **VII-5: $\text{BrO}_3^-$**



- **stable**
- **can be used as primary standard**
- **indirect titration**
- **used for the determination of certain special groups of organic compounds (e.g., olefinic, aromatic functional groups, hydroxyl, carbonyl, amine groups). (Example 17-7)**

## Reactions:



# Summary

## ✓ Reagents for redox titration

- Selection and preparation of standard solutions
- Properties (e.g., stability) of redox reagents
- Indicators
- Reactions (e.g., stoichiometry, pH dependence)

## ✓ Applications

- Redox reactions and equations
- Primary applications
- All related calculations

## ✓ Calculations

- Weight and concentrations of standards
- Weight and concentrations of analytes

# ***Homework***

**16-A, 1, 2, 6, 13**