# Fundamentals of Analytical Chemistry

Chapter 20

Applications of Oxidation/Reduction Titrations

## Problems

- 1, 5, 8, 15, 19, 28-34 even, 35, 39-41, 43, 45, 46, 51

## Auxiliary Reducing Reagents

- For a redox analysis, we must insure that the analyte is in the proper oxidation state
- Reductors
  - Jones reductor
    - Amalgamated zinc column
    - Reduces the amount of $H_2$ gas released by the reaction of metallic zinc
  - Walden reductor
    - Ag/AgCl column
    - Slightly milder than the Jones reductor
    - Table 20-1

## Standard Reducing Agents

- Iron(II)
  - Often used for back titration
  - Analyte reacts with Fe(II) to form Fe(III)
  - Excess Fe(II) titrated
- Sodium thiosulfate
  - Used in conjunction with iodine
    - Iodometry
    - More later

## Titrations with Oxidizing Agents

- Cerium (IV)
  - Note formal potentials vary from 1.70 to 1.44
    - Typically use 1.44 (1M $H_2SO_4$)
    - Solutions in the other acids not as stable as sulfuric
  - Primary standard
  - Must use redox indicator
- Permanganate
  - Similar applications to Ce(IV)
    - Not as stable as Ce(IV)
    - Cannot be used with chloride

## Titrations with Oxidizing Agents

- Permanganate
  - Advantages
    - Self-indicating
    - Inexpensive
- Only one viable permanganate ½ reaction for titrations
  - $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
  - Must titrate into a strongly acidic solution
    - If not, then other undesirable ½ reactions may occur

## Titrations with Oxidizing Agents

- Potassium Dichromate
  - Reduced to Cr(III)
  - Primary Standard
  - Must use indicator
    - Color of dichromate not intense enough for endpoint
- Iodine
  - Must dissolve in $I^-$ (to form triiodide ion)
  - Iodimitry – titration with $I_3^-$ ion
  - Use starch as the endpoint indicator.

## Titrations with Oxidizing Agents

- Iodometry
  - Analyte reacts with $I^-$ to form $I_3^-$
  - $I_3^-$ determined by titration with thiosulfate