Chemistry 4631

Instrumental Analysis
Lecture 21

Electroanalytical Chemistry

Oxidation/Reduction Reactions

- Transfer of electrons in solution from one reactant to another.
  - $Ce^{+4} + Fe^{+2} \rightarrow Ce^{+3} + Fe^{+3}$ (Redox Equation)
  - Ce^{+4} and Fe^{3+} (oxidizing agents)(e- acceptor)
  - Fe^{2+} and Ce^{3+} (reducing agents)(e- donor)
  - Ce^{4+} is reduced to Ce^{3+}
  - Fe^{2+} is oxidized to Fe^{3+}

- Redox equations can be split into two half reactions:

$$Ce^{+4} + e^{-} \rightarrow Ce^{+3} \quad \text{(red)}$$

$$Fe^{+2} \rightarrow Fe^{+3} + e- \quad \text{(ox)}$$

$$Ce^{+4} + Fe^{+2} \rightarrow Ce^{+3} + Fe^{+3}$$

Electroanalytical Chemistry

How to balance Redox equations

$MnO_4^- + NO_2^- \rightarrow Mn^{+2} + NO_3^-$

Total charge = -2 Total charge = +1

Charges do not balance - need to balance equation

Electroanalytical Chemistry

1. Write and balance half reactions separately

$MnO_4^- \rightarrow Mn^{+2}$ (need oxygen -- add H_2O)

$MnO_4^- \rightarrow Mn^{+2} + 4H_2O$ (balance O with H_2O)

$MnO_4^- + 8H^+ \rightarrow Mn^{+2} + 4H_2O$

(balance H with H^+)

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{+2} + 4H_2O$

(balance charge with electrons)

Electroanalytical Chemistry

1. Write and balance half reactions separately, con't

$NO_2^- \rightarrow NO_3^-$

$NO_2^- + H_2O \rightarrow NO_3^-$

$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+$

$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^-$

Electroanalytical Chemistry

2. Combine half reactions to form final redox equation

$(MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{+2} + 4H_2O) \times 2$

$(NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^-) \times 5$

$5NO_2^- + 2MnO_4^- + 5H_2O + 16H^+ + 10e^- \rightarrow 5NO_3^- + 2Mn^{+2} + 8H_2O + 10H^+ + 10e^-$

$5NO_2^- + 2MnO_4^- + 6H^+ \rightarrow 5NO_3^- + 2Mn^{+2} + 3H_2O$

Electroanalytical Chemistry

Electrochemical cells consist of electrodes immersed in an electrolyte solution.

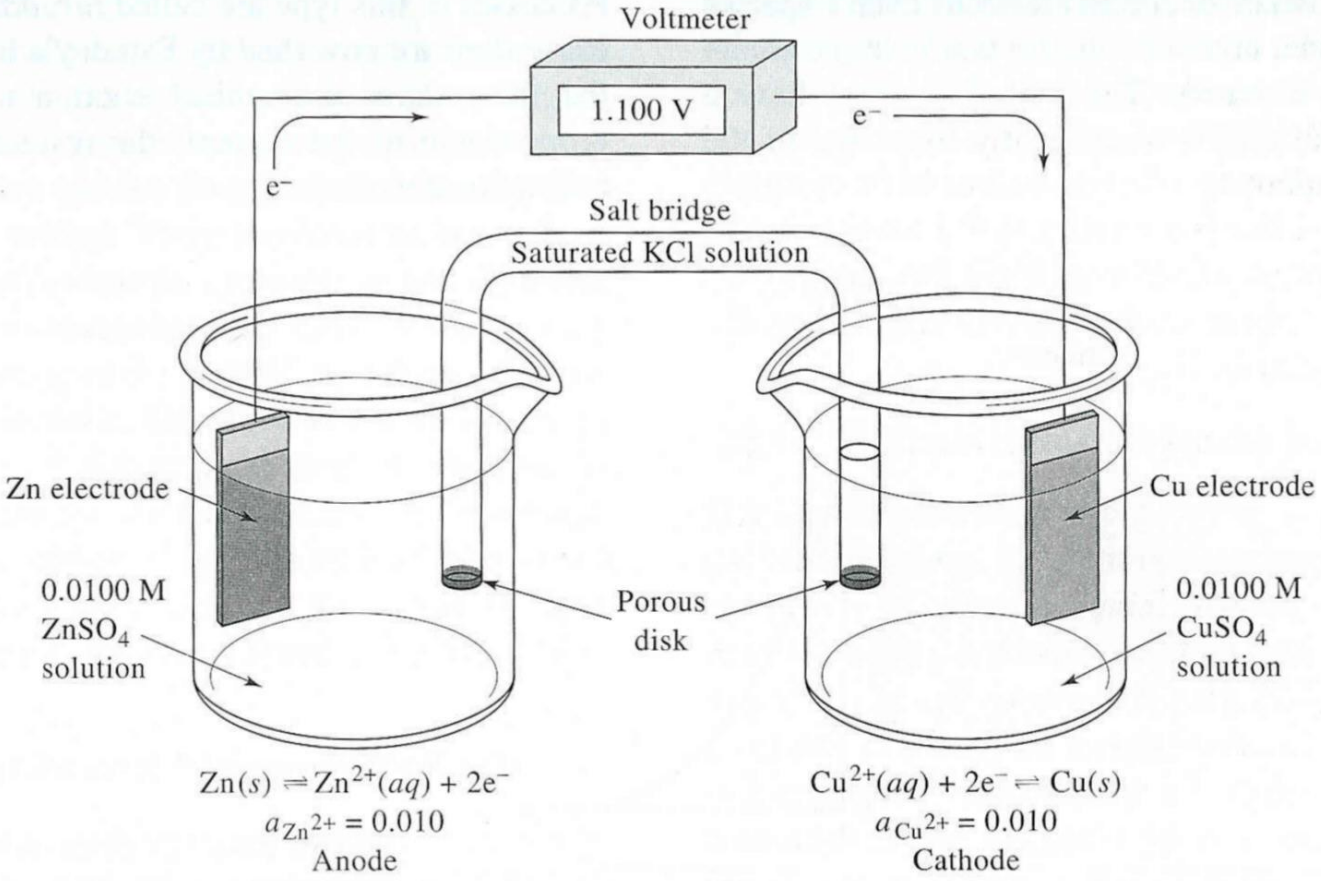


Figure 22-1 A galvanic electrochemical cell with a salt bridge.

Electroanalytical Chemistry

Conduction in a cell

Charge is conducted by:

- The electrodes and leads – involves electrons
- The solution – involves migration of cations and anions
- The interface – involves oxidation and reduction

Electroanalytical Chemistry

Solution structure

The double layer consist of

- Compact Inner layer where potential decreases linearly with distance from the electrode surface
- A diffuse layer where potential decreases exponentially

Electroanalytical Chemistry

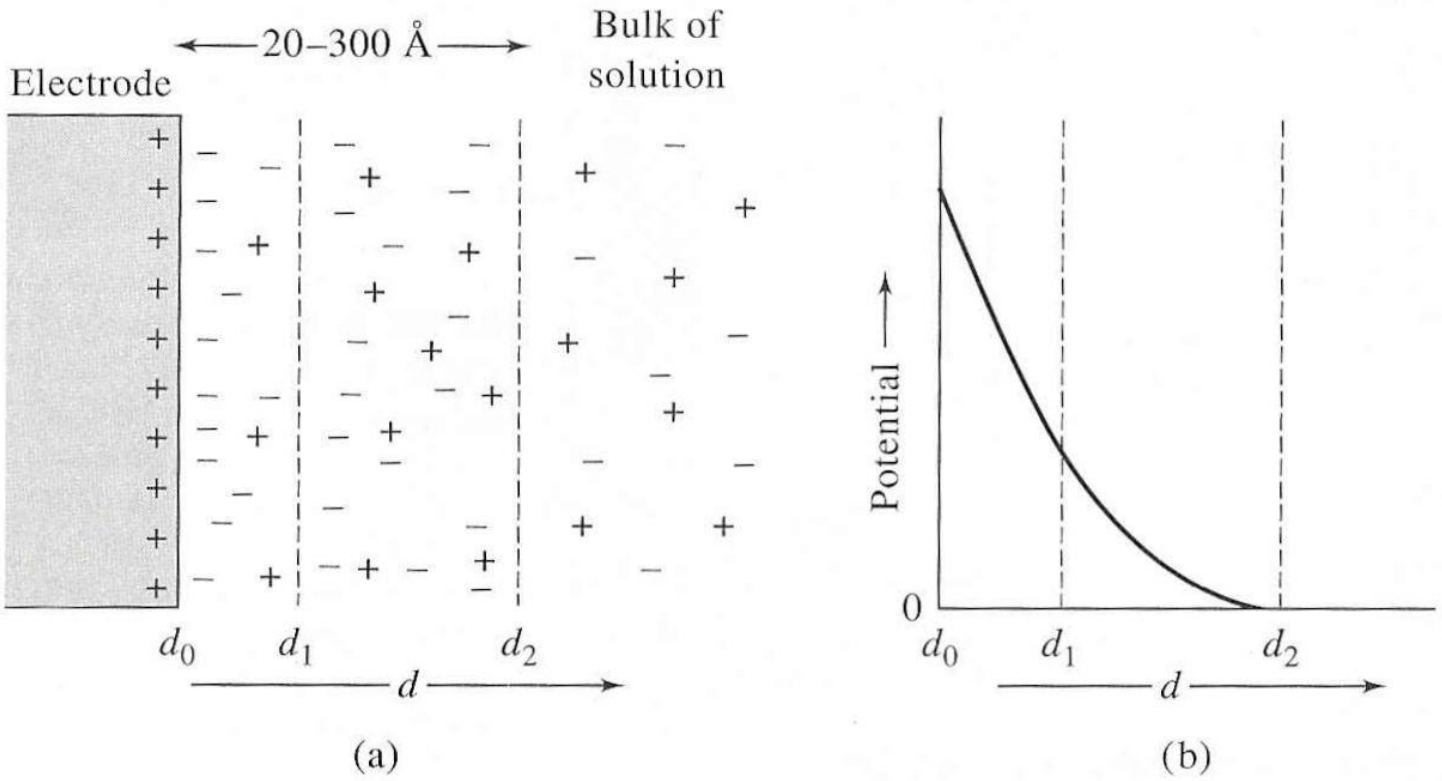


Figure 22-2 Electrical double layer formed at electrode surface as a result of an applied potential.

Electroanalytical Chemistry

Faradaic and Nonfaradaic currents

- Faradaic processes – direct transfer of electrons by an oxidation or reduction reaction.
- Obeys Faradays law – the amount of chemical reactant at an electrode is proportional to the current. (faradaic current).
- Nonfaradaic current – background current.

Electroanalytical Chemistry

Type of cells

Galvanic – cells that produce electrical energy (voltaic) -- i.e. battery

- stores electrical energy. Reactions at the electrodes proceed spontaneously.

Electrolytic – cells that consume electrical energy

- consumes energy. Need an external source of electrolytic energy

Type of electrodes

Cathode – electrode where reduction occurs

Anode – electrode where oxidation occurs

Electroanalytical Chemistry

Cell notation - Represent electrochemical cells by a shorthand method:

$$Cu \;|\; Cu^{+2}\,(0.0200M) \;\|\; Ag^{+}(0.0200M) \;|\; Ag$$

Anode	phase boundary (interface) potential occurs here	2 phase boundaries at either end of the salt bridge liquid junction potential.	phase boundary	cathode

Anode on left

Cathode on right

Single vertical line – represent phase boundary where potential may develop.

Double vertical line – represent junction between half cells.

Electroanalytical Chemistry

Strength of Oxidants and Reductants

$$2H^+ + Cd(s) \rightarrow H_2(g) + Cd^{+2}$$

$$2Ag^+ + H_2(g) \rightarrow 2Ag(s) + 2H^+$$

$$Cd^{+2} + Zn(s) \rightarrow Cd(s) + Zn^{+2}$$

(reactions proceed to the right)

Which species is the strongest oxidant (oxidizing agent)?

$H^+ > Cd^{2+}$ $\quad$ $Ag^+ > H^+$ $\quad$ $Cd^{2+} > Zn^{2+}$

List the order of oxidizing power:

$Ag^+ > H^+ > Cd^{+2} > Zn^{+2}$

Electroanalytical Chemistry

$2H^+ + 2e^- \text{ <---> } H_2(g)$

- Reaction at cathode when there is no easily reduced species.

$2H_2O \text{ <---> } O_2(g) + 4H^+ + 4e^-$

- Reaction at anode when there is no easily oxidized species.

Inert electrode, such as Pt is used when the reaction contains no solid metal.

Electroanalytical Chemistry

- Write the diagram for a cell that has a hydrogen electrode on the left, an iron(III)/iron(II) electrode on the right, and includes a salt bridge.

$Pt(s) \mid H_2(g) \mid H^+(aq) \parallel Fe^{3+}(aq), Fe^{2+}(aq) \mid Pt(s)$

Electroanalytical Chemistry

Write the chemical equation for the cell reaction resulting from the following half-reactions:

$H_2(g) \text{ ---> } 2H^+(aq) + 2e^-$

$Co^{3+}(aq) + 1e^- \text{ ---> } Co^{2+}(aq)$

Assume that platinum electrodes are used and write the cell diagram.

$H_2(g) + 2Co^{3+}(aq) \text{ ---> } 2H^+(aq) + 2Co^{2+}(aq)$

$Pt(s) \mid H_2(g) \mid H^+(aq) \parallel Co^{3+}(aq), Co^{2+}(aq) \mid Pt(s)$

Electroanalytical Chemistry

Electrode Potentials

Potential difference between cathode and anode of the cell is a measure of the tendency of the reaction. (like K for a chemical reaction)

We cannot determine absolute electrode potentials but we can determine relative electrode potentials (cannot just measure half a cell)

Electroanalytical Chemistry

Potential of a cell = $E_{cathode}$ - E_{anode} (half-reaction)

To generate the relative half -cell potentials use a standard.

i.e. Standard hydrogen reference electrode

(SHE or NHE).

This is the standard reference half-cell to measure all other half-reactions against.

Electroanalytical Chemistry

Standard Hydrogen Reference Electrode

SHE is a Gas electrode, made up of:

- Metal piece - Pt coated with platinum black (large surface area). Pt is in aqueous acid solution (HCl = 1M). Solution is saturated with H_2 (bubble) P=1atm. Metal is site of e^- transfer only.

Half reaction for SHE is : $2H^+(aq) + 2e^- \rightarrow H_2(g)$

Electroanalytical Chemistry

Standard Hydrogen Reference Electrode

Half reaction for SHE is : $2H^+(aq) + 2e^- \rightarrow H_2(g)$

Shorthand: Pt, H_2(p=1.00atm) | ([H^+] = 1.00M) || (25°C)

can be the anode or cathode.

This half-reaction is assigned 0.00V.

Half-wave potential are always written as reduction reactions.

i.e. SHE is the anode, other is the cathode.

Electroanalytical Chemistry

Standard Hydrogen Reference Electrode

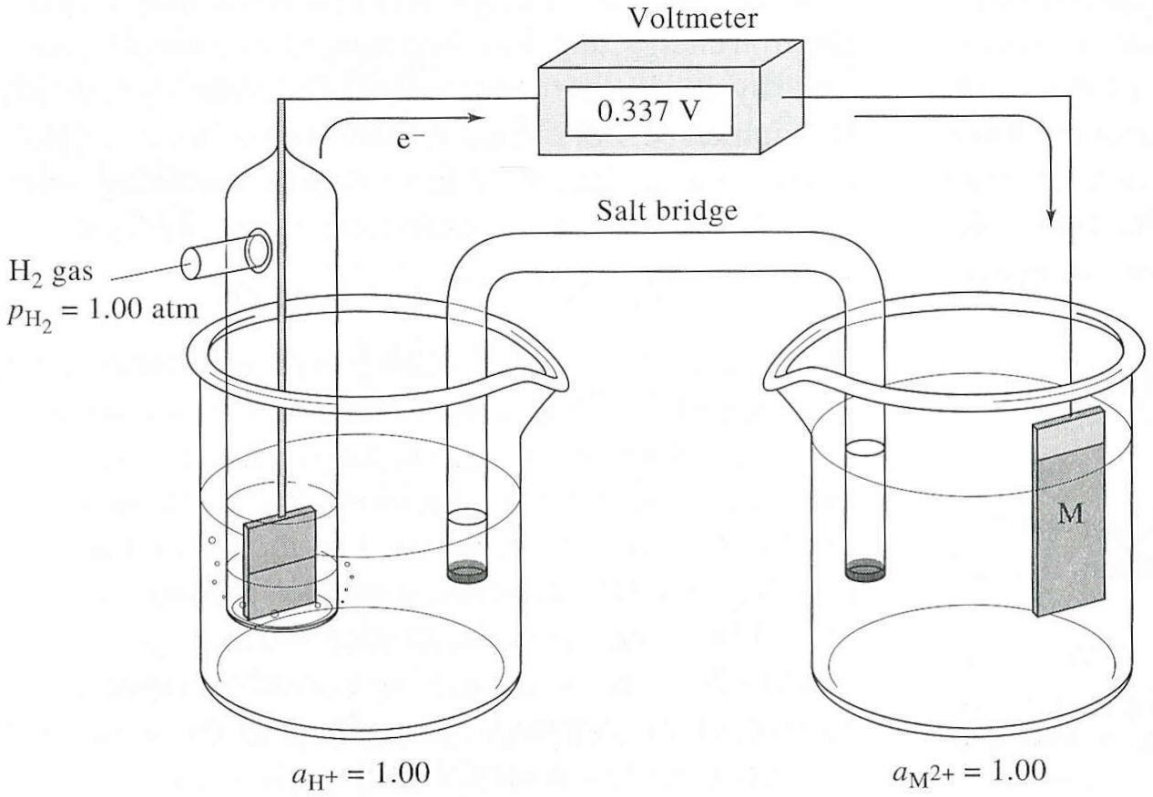


Figure 22-5 Definition of the standard electrode potential for $M^{2+}(aq) + 2e^- \rightleftharpoons M(s)$.

Electroanalytical Chemistry

Standard electrode potential represented by E^0

For a half-reaction, E^0 is defined when all activities are at unity.

Pt, H_2(p=1.00atm) | H^+ (a_{H+}= 1.00) || Ag+(a_{Ag+}=1.00) | Ag

$E_{cell} = 0.799V$ E^0 for Ag = 0.799V

$E_{cell} = E_{cathode} - E_{anode}$

$0.799 = 0.799 - 0$

$Ag^+ + e^- \rightarrow Ag(s)$ $E^0 = +0.799V$

Electroanalytical Chemistry

Sign Convention for Electrode Potentials (IUPAC)

Electrode potential is for half-reactions written as reductions.

Determined by the actual sign obtained when coupled with SHE in a galvanic cell.

Electroanalytical Chemistry

Sign Convention for Electrode Potentials (IUPAC)

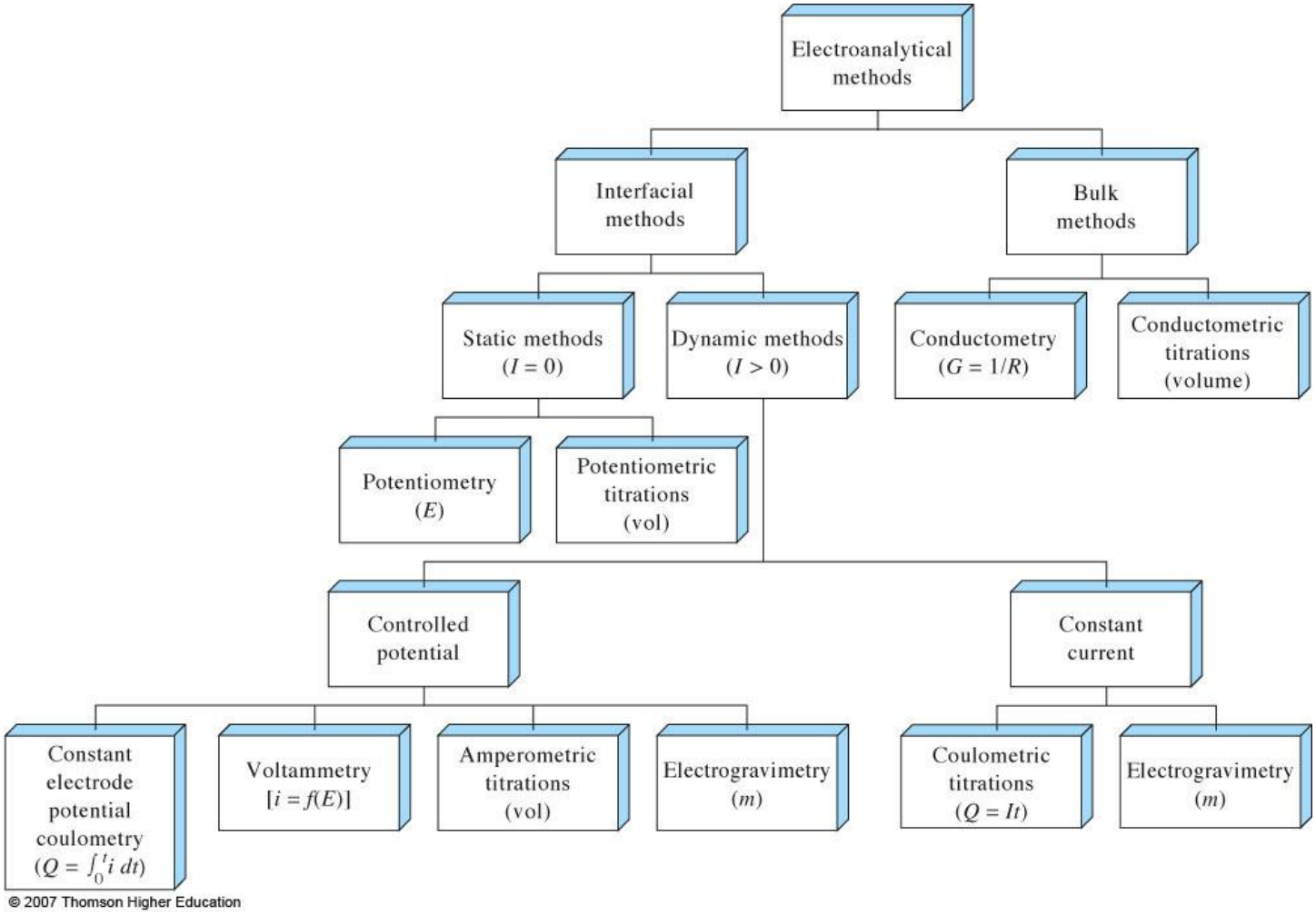
Sign of the electrode potential, E^0 ,

- is positive when the half-cell behaves spontaneously as the cathode.
- is negative when the half-cell behaves as an anode.
- is a measure of driving force for the half-reaction.

Positive sign - Cathodic (red) reaction is spontaneous.

Electroanalytical Chemistry

Types of Electroanalytical Methods



Assignment

- Read Chapter 10
- HW11 Chapter 10: 1, 2, 6-11
- HW11 Due 3-20

- Read Chapter 22
- HW12 Chapter 22: 1, 5, 7, 9, and 11
- HW12 Due 3-20