Electroanalytical Chemistry

- Electroanalytical chemistry encompasses a group of quantitative analytical methods that are based upon the electrical properties of an analyte solution when it is made part of an electrochemical cell.
- These methods make possible the determination of a particular oxidation state of an element.

$$Ox + ne^- \leftrightarrow Red$$

- There are two general types of electrochemical methods: potentiometric (no current, equilibrium potential) and voltammetric (current measured as a function of the applied potential.

Electrochemical Cells

Electrochemical cells consist of two electrodes: an **anode** (the electrode at which the oxidation reaction occurs) and a **cathode** (the electrode at which the reduction reaction occurs).

$$\mathbf{Cu(s) + Zn^{+2} \leftrightarrow Cu^{+2} + Zn(s)}$$

$$Cu(s) \leftrightarrow Cu^{+2} + 2e^{-} \text{ (oxidation)}$$

$$Zn^{+2} + 2e^{-} \leftrightarrow Zn(s) \text{ (reduction)}$$

There are two types of electrochemical cells: **galvanic** (ones that spontaneously produce electrical energy) and **electrolytic** (ones that consume electrical energy).

Electrochemical Potentials

We use concentrations in the Nernst equation, but really activities are the proper term. The **activity** of a species can be defined as the ability of a species to participate an equilibrium reaction involving itself.

e.g. $Fe^{+3} + e^- \leftrightarrow Fe^{+2}$ $FeCl^{+2}$, etc.

Depends on ionic strength

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

$$\Delta G_{rxn} = - nFE_{cell}$$

$$\Delta G_{rxn} = -RTlnK_{eq}$$

Key equations

Electrified Interfaces

$q^{metal} = -q^{solution}$ charge neutrality!

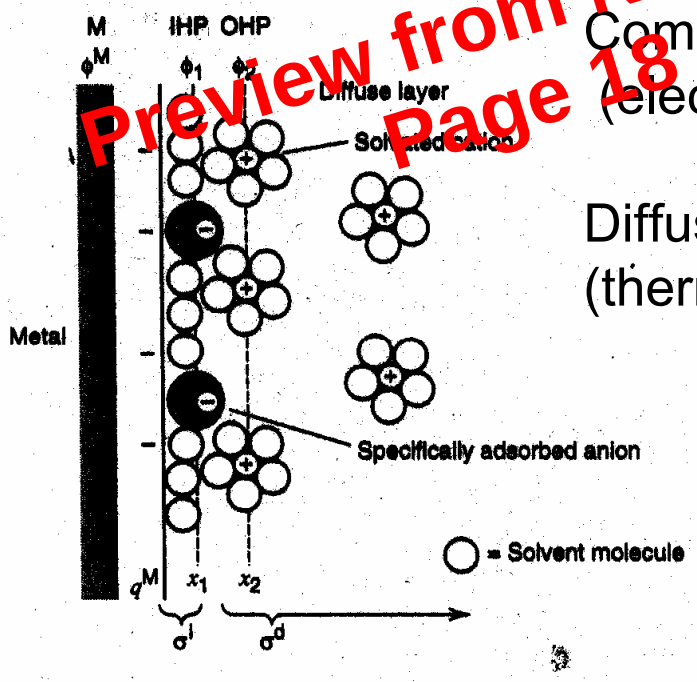

Figure 1.2.3 Proposed model of the double-layer region under conditions where anions are specifically adsorbed.

Compact Layer = inner and outer Helmholtz planes (electrostatic forces are very strong!)

Diffuse Layer = gradient of charge accumulation (thermal agitation)

$\sigma^{metal} = q^{metal}/area$ ($\mu C/cm^2$)

The excess charge on a metal is confined to the near surface region. However, the balancing charge on the solution side of the interface extends out into the solution with some thickness. (ionic zones in sol.)