

Chapter 22 – Introduction to Electroanalytical Chemistry

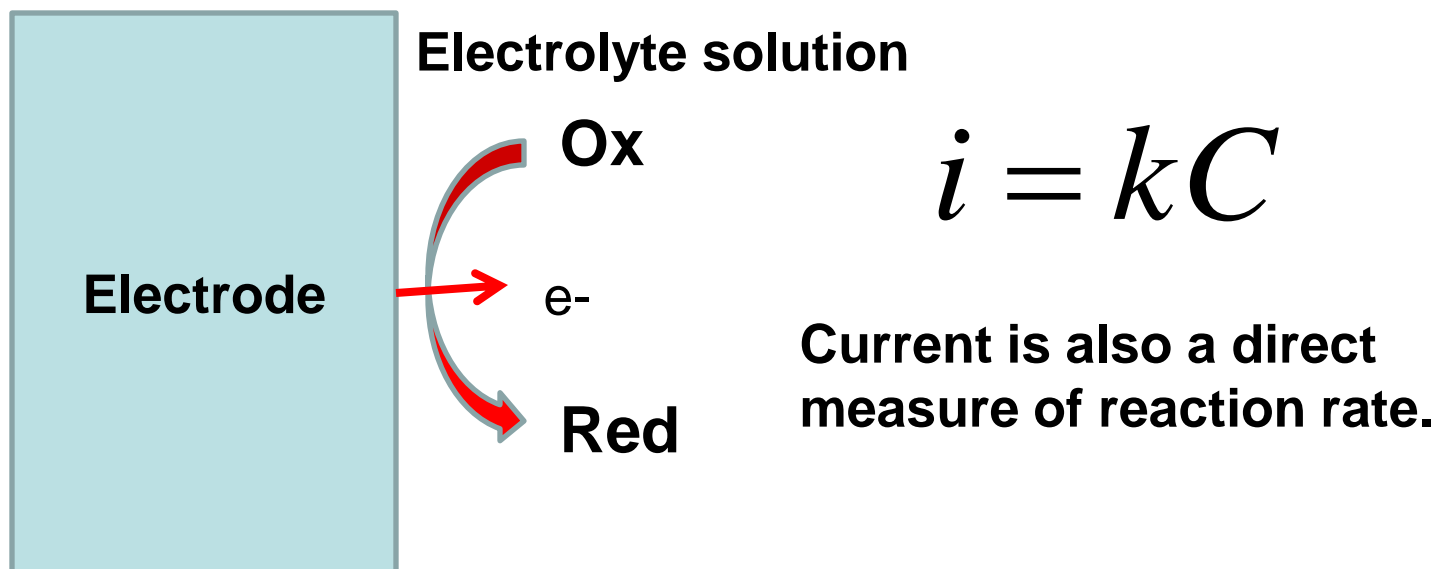
Read: pp. 628-653

Problems: 2,3,8,9

- **Electroanalytical methods** are a class of techniques in analytical chemistry, which study an analyte by measuring the potential (volts) and/or current (amperes) in an electrochemical cell containing the analyte.
- The three main categories are potentiometry (the difference in electrode potentials is measured), coulometry (the cell's current is measured over time), and voltammetry (the cell's current is measured while actively altering the cell's potential).

Electroanalytical Measurements

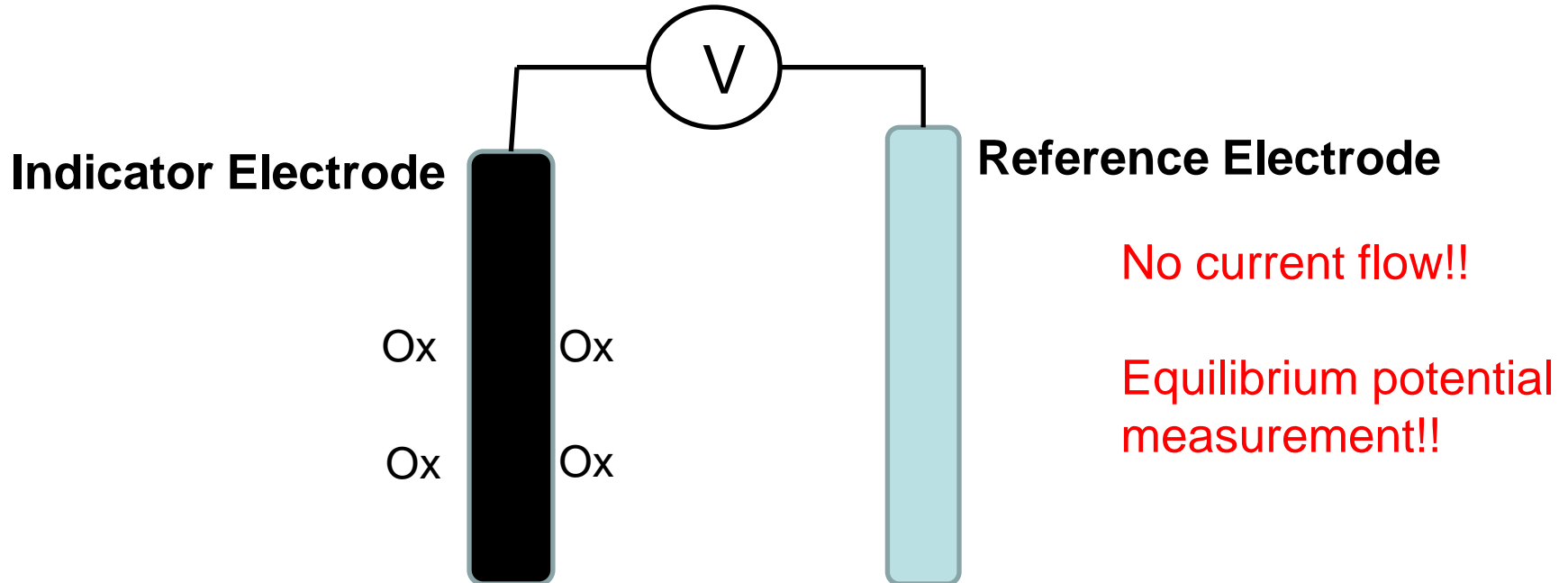
Electrochemical (analytical measurements) are *heterogeneous* in nature.



Important factors: electrode material, electrolyte solution, surface cleanliness, and surface chemistry

Potentiometric Measurements

Potentiometry passively measures the potential of a solution between two electrodes, affecting the solution very little in the process. The potential is then related to the concentration of one or more analytes.

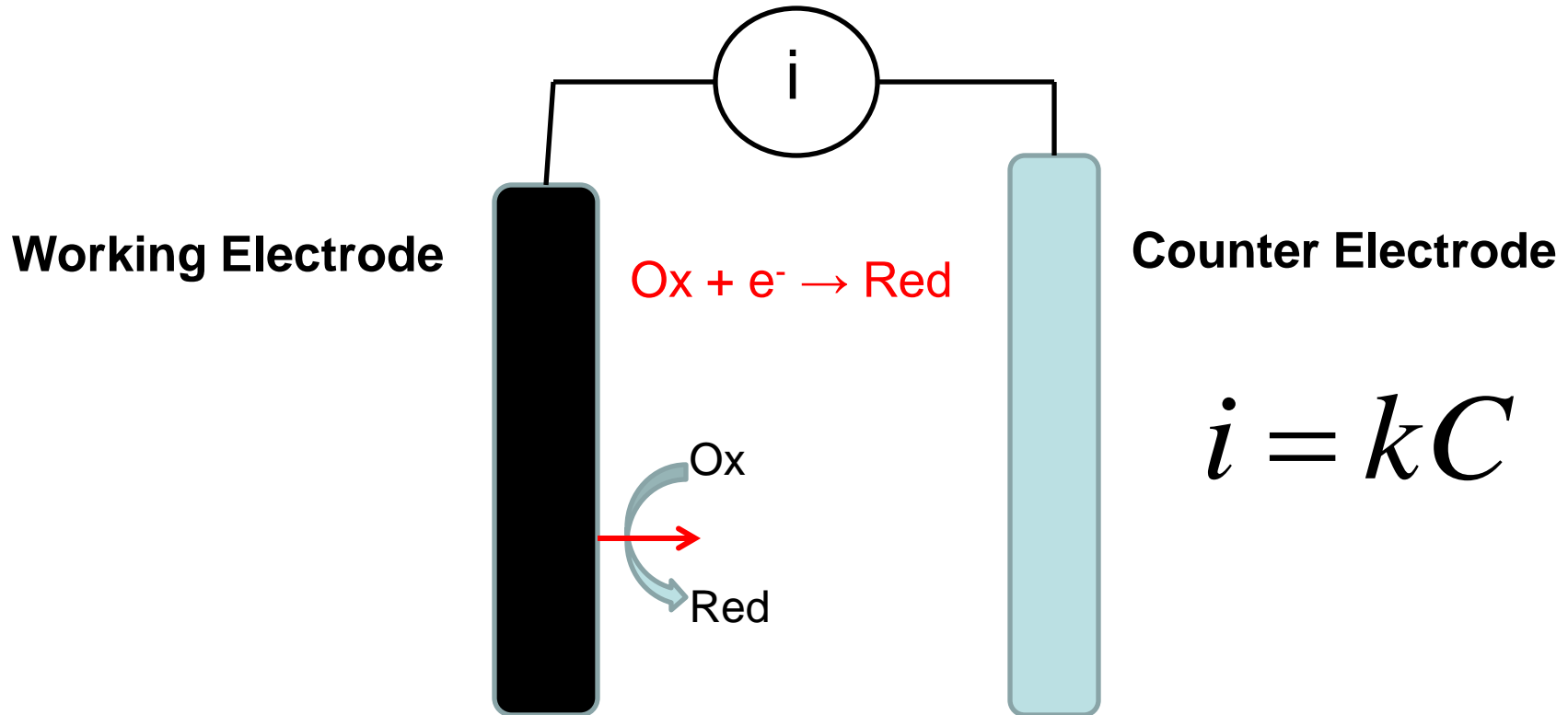


$$E_{ind}(vs.ref) = L + \frac{0.0592}{z} \log[Ox]$$

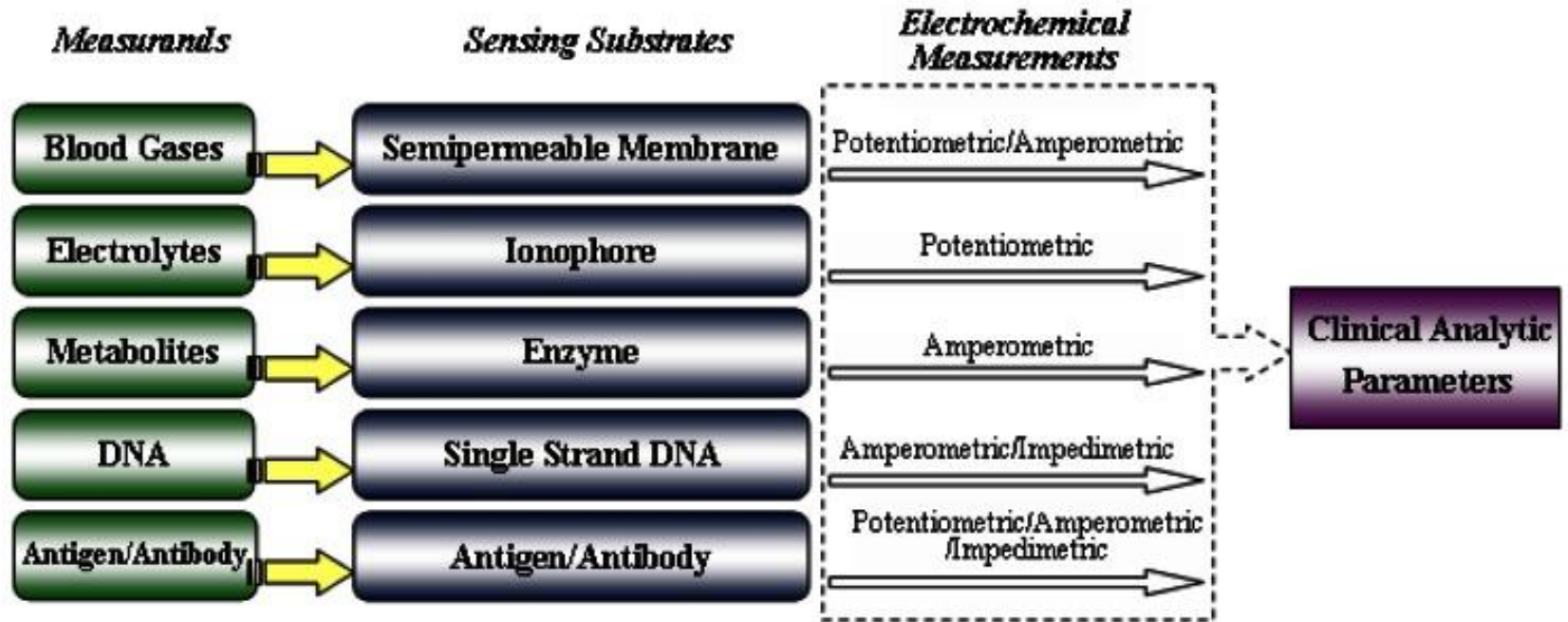
Examples: pH measurement, ion selective electrodes, gas sensing electrodes

Voltammetric Measurements

Voltammetry applies a constant and/or varying potential at an electrode's surface and measures the resulting current with a three electrode system. This method can reveal the [reduction potential](#) of an analyte and its [electrochemical reactivity](#). This method in practical terms is nondestructive since only a very small amount of the analyte is consumed at the two-dimensional surface of the [working](#) and [counter electrodes](#).



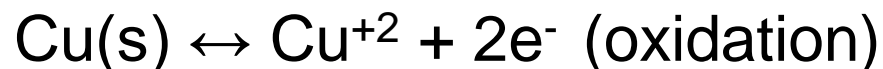
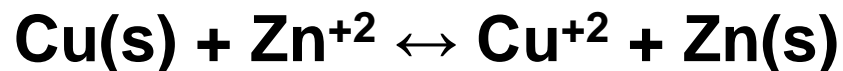
Electrochemical Sensors for Clinical Analysis



Various electrochemical sensors can be used to measure important analytes in blood. They tend to be inexpensive, robust, sensitive and selective with the proper surface modification.

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).



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

Electrochemical Cells

Conduction

1. Metals
2. Solution (ion migration)
3. Electrode rxns (at interfaces)

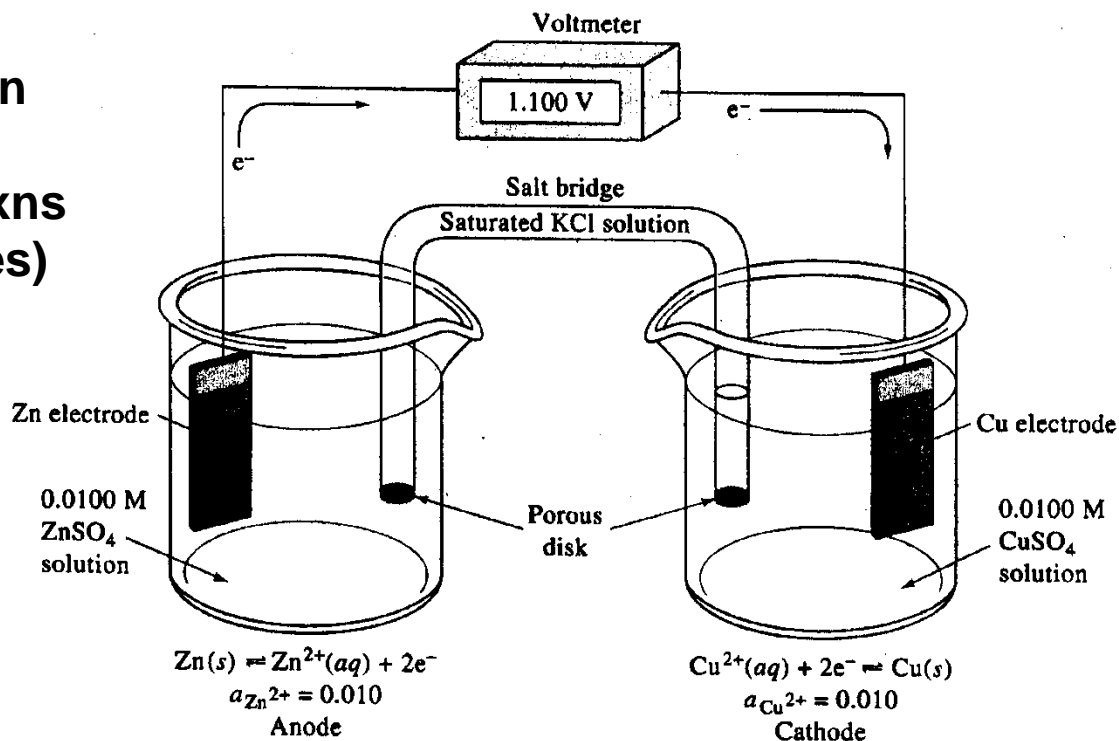


Figure 22-1 A galvanic electrochemical cell with a salt bridge.

A potential difference between two electrodes represents a tendency for the reaction to occur!

Electrochemical Potentials

The potential that develops in a cell is a measure of the tendency for a reaction to proceed toward equilibrium.

$$E = E^{o'} + \frac{2.303 RT}{nF} \log \frac{[\text{Ox}]}{[\text{Red}]}$$

Measured
E vs. Ref

Nernst Equation

$$a_x = \gamma [x]$$

Standard reduction reactions: all relative to the H_2/H^+ reaction, 298 K, unit activities for all species, and pH 0.

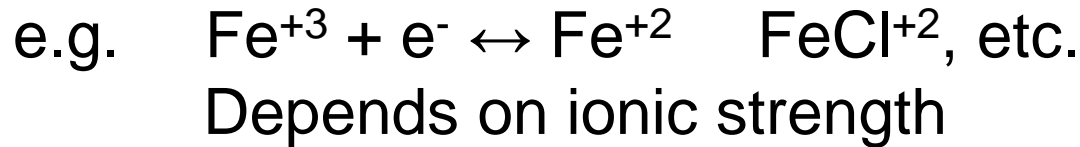
TABLE 22-1 Standard Electrode Potentials*

Reaction	E^0 at 25°C, V
$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-$	+1.359
$\text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$	+1.229
$\text{Br}_2(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{Br}^-$	+1.087
$\text{Br}_2(\text{l}) + 2\text{e}^- \rightleftharpoons 2\text{Br}^-$	+1.065
$\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}(\text{s})$	+0.799
$\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$	+0.771
$\text{I}_3^- + 2\text{e}^- \rightleftharpoons 3\text{I}^-$	+0.536
$\text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$	+0.337
$\text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{e}^- \rightleftharpoons 2\text{Hg}(\text{l}) + 2\text{Cl}^-$	+0.268
$\text{AgCl}(\text{s}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s}) + \text{Cl}^-$	+0.222
$\text{Ag}(\text{S}_2\text{O}_3)_2^{3-} + \text{e}^- \rightleftharpoons \text{Ag}(\text{s}) + 2\text{S}_2\text{O}_3^{2-}$	+0.010
$2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$	0.000
$\text{AgI}(\text{s}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s}) + \text{I}^-$	-0.151
$\text{PbSO}_4(\text{s}) + 2\text{e}^- \rightleftharpoons \text{Pb}(\text{s}) + \text{SO}_4^{2-}$	-0.350
$\text{Cd}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cd}(\text{s})$	-0.403
$\text{Zn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Zn}(\text{s})$	-0.763

*See Appendix 3 for a more extensive list.

Electrochemical Potentials

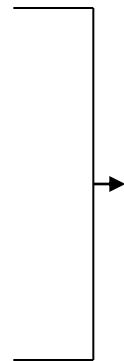
We use concentrations in the Nernst equation, but really activities are the proper term. The **activity** of a species can be defined as the ability of a species to participate an equilibrium reaction involving itself.



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

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

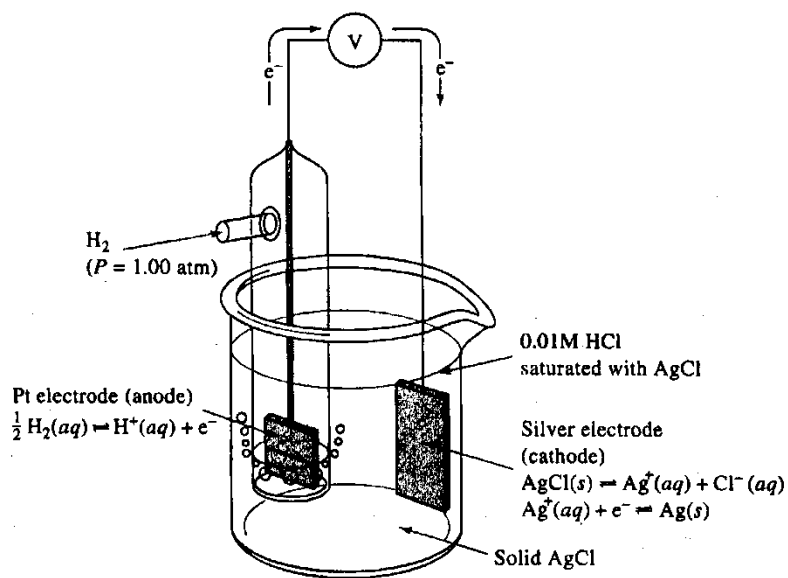
$$\Delta G_{\text{rxn}} = -RT \ln K_{\text{eq}}$$



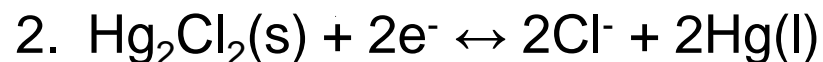
Key equations

Reference Electrodes

All cell potential measurements require two electrodes!



$$E = E^\circ + (0.059/n) \log 1/[\text{Cl}^-]$$



$$E = E^\circ + (0.059/2) \log 1/[\text{Cl}^-]^2$$

Figure 22-3 A galvanic cell without a liquid junction.

n = number of electrons transferred per mole, $2.303 RT/F = 0.059 \text{ V}$

Electrochemical Cells

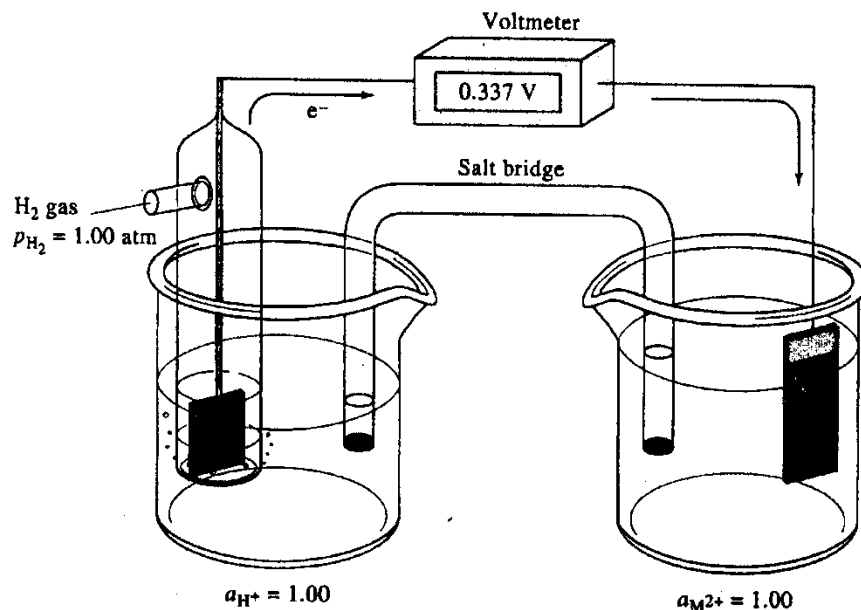
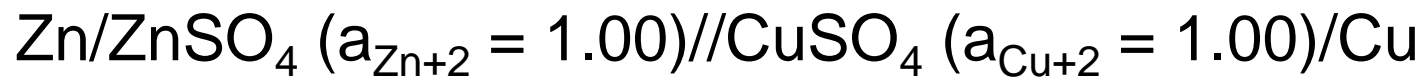
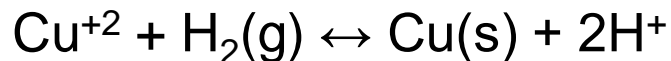


Figure 22-5 Definition of the standard electrode potential for $\text{M}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{M}(\text{s})$.



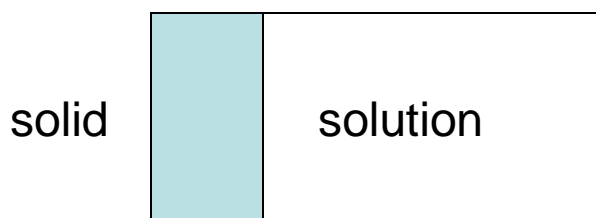
Anode (oxidation)

Cathode (reduction)

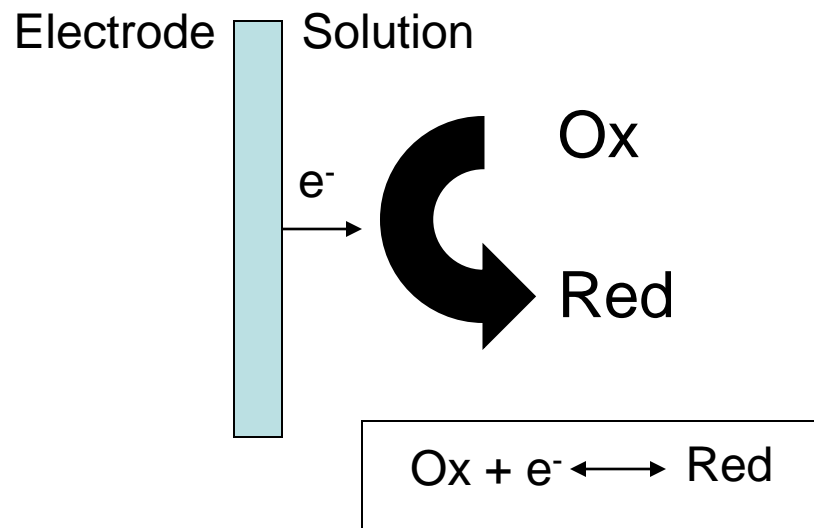
This shorthand is not always used in your textbook.

Electrochemical Cells and Reactions

Electrode (conductor) – Electrolyte (ionic solution)



Electrodes: Pt, Au, Pd, C, Hg



Electrolyte solutions (low ohmic resistance):
ionic solutions (NaCl), molten salts, and
ionic polymers (Nafion).

Electrode reaction kinetics are affected by the electrode surface cleanliness, surface microstructure, and surface chemistry.

Junction Potentials

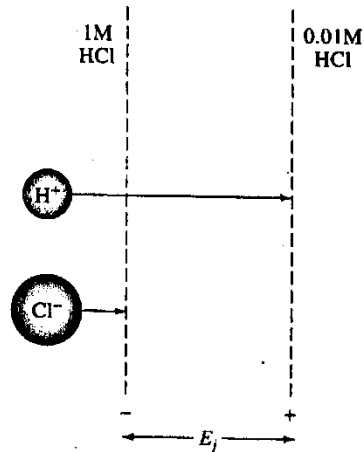


Figure 22-4 Schematic representation of a liquid junction showing the source of the junction potential E_j . The length of the arrows corresponds to the relative mobility of the two ions.

Differences in ion mobility give rise to junction potentials.
Unequal distribution!

Potentials develop anytime there is charge separation!

Ions move in the presence of an electric field.

1:1 electrolytes are normally homogeneous in a solution and there is no charge separation.

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} + E_j$$

Equilibrium vs. Non-equilibrium Electrochemical Measurements

Potentiometric = (0 net current measurements, stable potential that reflects activity of a reactant near the electrode surface.)

Voltammetric = (a current flows in response to an applied potential.)

When currents flow, net reactions take place. Since there are two electrodes (a working and a counter electrode), an oxidation reaction occurs at the anode and a reduction reaction occurs at the cathode.

Current (A=coulomb/sec) is a direct measure of the rxn. rate!

Currents in Electrochemical Cells

When currents are allowed to flow in electrochemical cells, this means that net reactions are taking place at each electrode. Equilibrium concentrations, as dictated by the Nernst equation are **not** necessarily achieved on the time-scale of the voltammetric measurement.

$E = iR$ where R is the resistance in the cell. Some types of resistance that can limit the current flow are charge-transfer resistance, mass transport resistance and solution ohmic resistance.

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} - iR$$

$i \propto kC$ where C is the analyte concentration

Currents in Electrochemical Cells

Remember = all electrochemical reactions take place at the electrode-solution interface!!

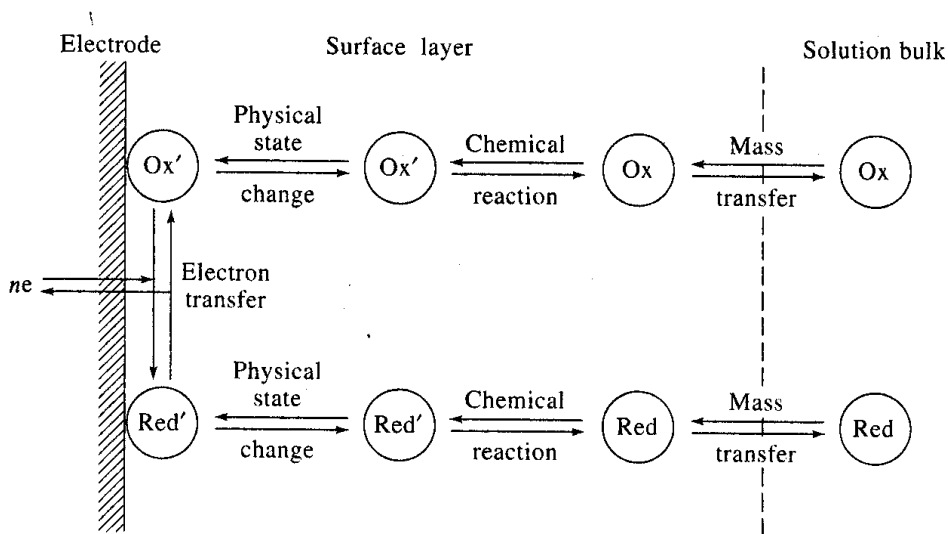


Figure 22-8 Steps in the reaction $\text{Ox} + n\text{e}^- \rightleftharpoons \text{Red}$ at an electrode. Note that the surface layer is only a few molecules thick. (Adapted from A. J. Bard and L. R. Faulkner, *Electrochemical Methods*, p. 21. New York: Wiley, 1980. Reprinted by permission of John Wiley & Sons, Inc.)

Current limited by (i) charge transfer resistance, (ii) mass transport resistance and ohmic solution resistance.

Modes of mass transport: (i) diffusion, (ii) convection and (iii) migration.

$$i \text{ (current)} = \partial Q / \partial t = nFA(\text{area, cm}^2)\partial C / \partial t \text{ (flux, mol/s-cm}^2)$$