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

\[ i = kC \]

Current is also a direct measure of reaction rate.
**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.

\[ E_{ind} (v s. \text{ref}) = L + \frac{0.0592}{z} \log[Ox] \]

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.

\[ i = kC \]
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).

\[
\text{Cu(s) + Zn}^{+2} \leftrightarrow \text{Cu}^{+2} + \text{Zn(s)}
\]

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

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

There are two types of electrochemical cells: **galvanic** (ones that spontaneously produce electrical energy) and **electrolytic** (ones that consume electrical energy).
A potential difference between two electrodes represents a tendency for the reaction to occur!
The potential that develops in a cell is a measure of the tendency for a reaction to proceed toward equilibrium.

\[ E = E^\circ + \frac{2.303 \, RT}{nF} \log \frac{[\text{Ox}]}{[\text{Red}]} \]

Nernst Equation

\[ a_x = \gamma \, [x] \]

Standard reduction reactions: all relative to the \( \text{H}_2/\text{H}^+ \) reaction, 298 K, unit activities for all species, and pH 0.

**TABLE 22-1 Standard Electrode Potentials**

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

*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.g. \( \text{Fe}^{3+} + e^- \leftrightarrow \text{Fe}^{2+} \quad \text{FeCl}^{+2}, \text{etc.} \)

Depends on ionic strength

\[
\begin{align*}
E_{\text{cell}} & = E_{\text{cathode}} - E_{\text{anode}} \\
\Delta G_{\text{rxn}} & = -nFE_{\text{cell}} \\
\Delta G_{\text{rxn}} & = -RT\ln K_{\text{eq}}
\end{align*}
\]

Key equations
Reference Electrodes

All cell potential measurements require two electrodes!

1. \( \text{AgCl}(s) + e^- \leftrightarrow \text{Ag}(s) + \text{Cl}^- \)
   \[ E = E^0 + \frac{0.059}{n} \log_1 \left[ \frac{1}{[\text{Cl}^-]} \right] \]

2. \( \text{Hg}_2\text{Cl}_2(s) + 2e^- \leftrightarrow 2\text{Cl}^- + 2\text{Hg}(l) \)
   \[ E = E^0 + \frac{0.059}{2} \log_1 \left[ \frac{1}{[\text{Cl}^-]^2} \right] \]

\( n = \text{number of electrons transferred per mole}, \ 2.303 \frac{RT}{F} = 0.059 \text{ V} \)

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

\[ \text{Cu}^{+2} + \text{H}_2(g) \leftrightarrow \text{Cu}(s) + 2\text{H}^+ \]

\[ \text{Zn/ZnSO}_4 \ (a_{\text{Zn}^{+2}} = 1.00)//\text{CuSO}_4 \ (a_{\text{Cu}^{+2}} = 1.00)/\text{Cu} \]

Anode (oxidation) Cathode (reduction)

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

This shorthand is not always used in your textbook.
Electrochemical Cells and Reactions

Electrode (conductor) – Electrolyte (ionic solution)

Electrodes: Pt, Au, Pd, C, Hg


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

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.

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

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

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.
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!!

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

\[ i \text{ (current)} = \frac{\partial Q}{\partial t} = nF A \text{(area, cm}^2) \frac{\partial C}{\partial t} \text{ (flux, mol/s-cm}^2) \]