Chapter 1. Introduction of Electrochemical Concepts

- **Electrochemistry** – concerned with the interrelation of electrical and chemical effects. Reactions involving the reactant – the *electron*.

  *Chemical changes caused by the passage of current*

- An electrochemical system is not *homogeneous* but is *heterogeneous*.

- Broad Field: electroanalysis, sensors, energy storage and conversion devices, corrosion, electrosynthesis, and metal electroplating.
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.

  \[
  \text{Ox} + n\text{e}^- \leftrightarrow \text{Red}
  \]

• 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).

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

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

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

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.
Electrochemical Potentials

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}^- + 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}(\text{S}_2\text{O}_3)^{3-} + e^- \rightleftharpoons \text{Ag}(s) + 2\text{S}_2\text{O}_3^{3-} )</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.

\[ \text{e.g. } Fe^{+3} + e^- \leftrightarrow Fe^{+2} \quad \text{FeCl}^{+2}, \text{ etc.} \]

Depends on ionic strength

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

Key equations
Reference Electrodes

All cell potential measurements require two electrodes!

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

2. \( \text{Hg}_2\text{Cl}_2(s) + 2e^- \leftrightarrow 2\text{Cl}^- + 2\text{Hg}(l) \)
   \[ E = E^o + (0.059/2) \log [\text{Cl}^-]^2 \]

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

\( E^o \) is the standard electrode potential
\( E \) is the cell potential

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

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

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

- **Anode (oxidation)**
- **Cathode (reduction)**

*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.
Electrochemical Cells and Reactions

Two electrified interfaces but only one of interest.

\[ V = \frac{J}{C} \] measure of the energy available to drive charge externally between electrodes.

Rate of oxidation = Rate of reduction

Reference electrode: \( \text{AgBr} + e^- \rightleftharpoons \text{Ag} + \text{Br}^-_{(aq)} \) \( E^0 = 0.071 \text{V} \) vs. NHE
Magnitude of the potential controls the direction and rate of charge transfer.

As a potential is moved negative, the species that will be reduced first (assuming all are rapid) is the oxidant (acceptor) in the couple with the least negative $E^0$.

Figure 1.1.2  Representation of (a) reduction and (b) oxidation process of a species, A, in solution. The molecular orbitals (MO) of species A shown are the highest occupied MO and the lowest vacant MO. These correspond in an approximate way to the $E^0$'s of the A/A$^-$ and A$^+/A$ couples, respectively. The illustrated system could represent an aromatic hydrocarbon (e.g., 9,10-diphenylanthracene) in an aprotic solvent (e.g., acetonitrile) at a platinum electrode.
There are two types of current flow:

1. **Faradaic** – charge transferred across the electrified interface as a result of an electrochemical reaction.

   \[
   Q = nFN \quad \text{and} \quad \frac{dQ}{dt} = i = nF \frac{dN}{dt}
   \]

2. **Non-faradaic** – charge associated with movement of electrolyte ions, reorientation of solvent dipoles, adsorption/desorption, etc. at the electrode-electrolyte interface. This is the background current in voltammetric measurements.
**Electrochemical Cells and Reactions**

**Pt/H⁺, Br⁻ (1M)/AgBr/Ag**

(+) current = cathodic
(-) current = anodic
(+) potential = left
(-) potential = right

**Figure 1.1.4** Schematic current-potential curve for the cell Pt/H⁺, Br⁻ (1 M)/AgBr/Ag, showing the limiting proton reduction and bromide oxidation processes. The cell potential is given for the Pt electrode with respect to the Ag electrode, so it is equivalent to $E_{Pt}$ (V vs. AgBr). Since $E_{Ag/AgBr} = 0.07$ V vs. NHE, the potential axis could be converted to $E_{Pt}$ (V vs. NHE) by adding 0.07 V to each value of potential.

$Br_2 + 2e^- \leftrightarrow 2Br^-$ \hspace{1cm} $E^0 = 1.09$ V vs. NHE

$2H^+ + 2e^- \leftrightarrow H_2$ \hspace{1cm} $E^0 = 0.00$ V vs. NHE

$E_{cell} = E_c - E_a$
Electrochemical Cells and Reactions

Hg/H⁺, Br⁻ (1M)/AgBr/Ag

Kinetically fast reactions have significant faradaic current flow near $E^\circ$, while sluggish reactions have little current flow except at large overpotentials.

$$Hg_2Br_2 + 2e^- \leftrightarrow 2Hg + 2Br^-$$

$E^\circ = 0.14 \text{ V vs. NHE}$

$$2H^+ + 2e^- \leftrightarrow H_2$$

$E^\circ = 0.00 \text{ V vs. NHE}$
Electrochemical Cells and Reactions

Hg/H^+, Br^- (1M), Cd^{2+}(1mM)/AgBr/Ag

\[ \text{CdBr}_4^{2-} + 2e^- \leftrightarrow \text{Cd(Hg)} + 4\text{Br}^- \]

\[ \text{Hg}_2\text{Br}_2 + 2e^- \leftrightarrow 2\text{Hg} + 2\text{Br}^- \quad E^0 = 0.14 \text{ V vs. NHE} \]

\[ 2\text{H}^+ + 2e^- \leftrightarrow \text{H}_2 \quad E^0 = 0.00 \text{ V vs. NHE} \]
Electrochemical Cells and Reactions

Figure 1.1.7  (a) Potentials for possible reductions at a platinum electrode, initially at −1 V vs. NHE in a solution of 0.01 M each of Fe^{3+}, Sn^{4+}, and Ni^{2+} in 1 M HCl. (b) Potentials for possible oxidation reactions at a gold electrode, initially at −0.1 V vs. NHE in a solution of 0.01 M each of Sn^{2+} and Fe^{2+} in 1 M HI. (c) Potentials for possible reductions at a mercury electrode in 0.01 M Cr^{3+} and Zn^{2+} in 1 M HCl. The arrows indicate the directions of potential change discussed in the text.
Electrified Interfaces

Ideally polarizable electrode (IPE) – no charge transfer across the interface. Ions move in and out of the interfacial region in response to potential changes. The interface behaves as a capacitor (charge storage device).

Excess electrons on one plate and a deficiency on the other.

Changing the potential, $E$, causes the charge stored, $Q$, to change according to the relationship:

$$Q(\text{coulombs}) = C(\text{farads}) \times E(\text{volts})$$
Electrified Interfaces

\[ q_{\text{metal}} = -q_{\text{solute}} \]

charge neutrality!

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

Diffuse Layer = gradient of charge accumulation
(thermal agitation)

\[ \sigma_{\text{metal}} = \frac{q_{\text{metal}}}{\text{area}} \, (\mu\text{C/cm}^2) \]

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.)
Electrified Interfaces

\[ \sigma_{\text{metal}} = - (\sigma_{\text{IHP}} + \sigma_{\text{OHP}} + \sigma_{\text{diffuse}}) \]

Structure of the electric double layer has a major effect on electrode reaction kinetics! (Faradaic reaction rates).

Species not specifically adsorbed approach the OHP.

\[ \Phi_2 - \Phi_s \] is wasted!!

\[ \Phi_m - \Phi_s \] is potential felt by analyte

Figure 1.2.4 Potential profile across the double-layer region in the absence of specific adsorption of ions. The variable \( \phi \), called the inner potential, is discussed in detail in Section 2.2. A more quantitative representation of this profile is shown in Figure 12.3.6.

Field strength \( \left( \frac{dy}{dx} \right)_{x = x_2} \) is critical!!
The solution side of the interface consists of a **compact layer** (inner and outer Helmholtz layers) plus a **diffuse layer**.

Diffuse layer extends from the OHP to the bulk solution. Ionic distribution influenced by ordering due to coulombic forces and disorder caused by random thermal motion.

\[ Q_m + (Q_{CL} + Q_{DL}) = 0 \]
\[ Q_m = - (Q_{CL} + Q_{DL}) \]

\[ Q = CE \]
\[ Q_{DL} = C_{dl}A(E-E_{pzc}) \]

\[ Q = CE \]
\[ Q_{DL} = C_{dl}A(E-E_{pzc}) \]

\[ 1/C_{TOT} = 1/C_{CL} + 1/C_{DL} \]

Smallest value dominates the interfacial capacitance.
Electrochemical Experiment and Variables in Electrochemical Cells

Figure 1.3.2 Variables affecting the rate of an electrode reaction.

Electrode pretreatment matters a great deal!!!
Electrochemical Experiment and Variables in Electrochemical Cells

1. Mass transfer of reactant/product to and away from the electrode interface.
2. Electron transfer at interface.
3. Preceeding or follow-up chemical reactions.
4. Surface processes (adsorption/desorption)

Figure 1.3.6 Pathway of a general electrode reaction.

Working Electrode (Indicator Electrode)
Electrochemical Experiment and Variables in Electrochemical Cells

$$\eta = E - E_{eq}$$

![Diagram of a three-electrode cell](image1.png)

Figure 1.3.10 Three-electrode cell and notation for the different electrodes.

$$i \text{ (amperes)} = \frac{dQ}{dt} \text{ (coulombs/s)}$$

$$\frac{Q}{nF \text{ (coulombs/mol)}} = N \text{ (moles electrolyzed)}$$

Rate (mol/s) = \frac{dN}{dt} = \frac{i}{nF}$$

Rate (mol/s-cm²) = \frac{i}{nFA}$$
Mass Transport

Modes of Mass Transport

1. **Migration** – movement of charged body under influence of an electric field.
2. **Diffusion** – movement of species under the influence of a concentration gradient.
3. **Convection** – stirring or hydrodynamic transport.

\[
J_i(x) = -D_i \frac{dC_i(x)}{dx} - \frac{z_i F}{RT} D_i C_i \frac{d\Phi(x)}{dx} - C_i \nu(x)
\]

- **\( J_i(x) \)** = flux of \( i \) (mol/s-cm²)
- **\( D \)** = diffusion coeff. (cm²/s)
- **\( C \)** = conc. (mol/cm³)
- **\( \frac{d\Phi(x)}{dx} \)** = potential gradient
- **\( z \)** = charge on species
- **\( \nu(x) \)** = velocity (cm/s)
Mass Transport

\[ l = (2Dt)^{1/2} \]

Diffusion layer thickness

\[ \nu_{mt} = D_o \left( \frac{dC_o}{dx} \right)_{x=0} \]

\[ \nu_{mt} = D_o \left( C^*_o \ - \ C_o(x=0) \right)/\delta_o \]

\[ D_o \left( C^*_o \ - \ C_o(x=0) \right)/\delta_o = i/nFA = D_r(C_r(x=0) \ - \ C^*_r)/\delta_r \]
Current-Voltage Curve Shapes

Figure 1.5.1 Effect of an irreversible following homogeneous chemical reaction on nernstian $i-E$ curves at a rotating disk electrode. (1) Unperturbed curve. (2) and (3) Curves with following reaction at two rotation rates, where the rotation rate for (3) is greater than for (2).