A.) Introduction:

1.) **Electroanalytical Chemistry**: group of analytical methods based upon electrical properties of analytes when it is made part of an electrochemical cell

2.) **General Advantages of Electrochemistry**:
   a) selective for particular redox state of a species e.g. $\text{Ce}^{\text{III}}$ vs. $\text{Ce}^{\text{IV}}$
   b) cost - $8,000 - $25,000 for a good instrument compared to $50,000 - $250,000 for a good spectrophotometer
   c) measures activity (not concentration)
      ② activity usually of more physiological importance
   d) fast
   e) in situ
   f) information about:
      ② oxidation states, ② stoichiometry, ② rates
      ② charge transfer, ② equilibrium constants
B.) Types of Electroanalytical Methods

- Electroanalytical methods
  - Interfacial methods
    - Static methods ($I = 0$)
    - Dynamic methods ($I > 0$)
  - Bulk methods
    - Conductometry ($G = 1/R$)
    - Conductometric titrations (volume)
  - Potentiometry ($E$)
    - Potentiometric titrations (vol)
  - Controlled potential
    - Constant electrode potential coulometry ($Q = \int_0^t i \, dt$)
  - Voltammetry [$i = f(E)$]
    - Amperometric titrations (vol)
  - Electrogravimetry ($m$)
  - Coulometric titrations ($Q = It$)
  - Electrogravimetry ($m$)
B.) Types of Electroanalytical Methods

Potentiometry: measure the potential of electrochemical cells without drawing substantial current
   Examples: pH measurements, ion-selective electrodes, titrations

Coulometry: measures the electricity required to drive an electrolytic oxidation/reduction to completion
   Examples: titrations, “chloridometers” (AgCl)

Voltammetry: measures current as a function of applied potential under conditions that keep a working electrode polarized
   Examples: cyclic voltammetry, many biosensors
C.) Electrochemical Cell:

1.) Basic Set-up:
   a) Two electrodes
   b) electrolytes solution
      1) external connection between electrodes (wire)
      2) internal connection via contact with a common solution or by different solutions connected by a salt bridge.

salt bridge – acts to isolate two halves of electrochemical cell while allowing migration of ions and current flow.

- usually consists of a tube filled with potassium chloride
- separate species to prevent direct chemical reactions
2.) **Conduction/Flow of current (charge) in cell:**

a) electrons \((e^-)\) within wires between two electrodes

b) ions within solution of each \(\frac{1}{2}\) cell (anions & cations) and through salt bridge/migration

c) electrochemical reactions at electrode surfaces

![Diagram of electrochemical cell](image)

At Cu electrode: \(\text{Cu}^{2+} + 2e^- \leftrightarrow \text{Cu(s)} \rightarrow \text{reduction} \) – gain of \(e^-\) net decrease in charge of species

At Zn electrode: \(\text{Zn(s)} \leftrightarrow \text{Zn}^{2+} + 2e^- \rightarrow \text{oxidation} \) – loss of \(e^-\) net increase in charge of species
3.) **Net Reaction in Cell** – sum of reactions occurring in the two $\frac{1}{2}$ cells

$$
\begin{align*}
Zn(s) & \leftrightarrow Zn^{2+} + 2e^- \\
Cu^{2+} + 2e^- & \leftrightarrow Cu(s) \\
Cu^{2+} + Zn(s) & \leftrightarrow Zn^{2+} + Cu(s)
\end{align*}
$$

**Potential of overall cell** = measure of the tendency of this reaction to proceed to equilibrium

*at equilibrium*, potential ($E_{cell}$) = 0

Larger the potential, the further the reaction is from equilibrium and the greater the driving force that exists

Similar in concept to balls sitting at different heights along a hill
4.) **Types of Cells:**

**Galvanic Cells** – reaction occurs naturally
- positive potential \( E_{\text{cell}} = + \)
- exothermic \( \rightarrow \) produces energy
4.) **Types of Cells:**

**Electrolytic Cells** – reaction does not occur naturally, requires external stimulus (energy) to occur

- negative potential ($E_{\text{cell}} = -$)
- endothermic → requires energy

**Chemically Reversible Cell** – a cell in which reversing the direction of the current simply reverses the chemical reaction
5.) **Electrodes:**

   a.) **Cathode** – electrode where *reduction* occurs
   
   **Anode** – electrode where *oxidation* occurs

   b.) Examples of cathode ½ reactions:
   
   \[
   \begin{align*}
   \text{Cu}^{2+} + 2e^- & \leftrightarrow \text{Cu}(s) \\
   \text{Fe}^{3+} + e^- & \leftrightarrow \text{Fe}^{2+} \\
   \text{AgCl}(s) + e^- & \leftrightarrow \text{Ag}(s) + \text{Cl}^- 
   \end{align*}
   \]
   
   - e\(^{-}\) supplied by electrical current via electrode
   
   - species (products/reactants) can both be in solution (Fe\(^{3+}/\text{Fe}^{2+}\)) solids or coated on electrodes (AgCl(s)/Ag(s) or combination (Cu\(^{2+}/\text{Cu}(s)\)

   c.) Examples of anode ½ reactions:
   
   \[
   \begin{align*}
   \text{Cu}(s) & \leftrightarrow \text{Cu}^{2+} + 2e^- \\
   \text{Fe}^{2+} & \leftrightarrow \text{Fe}^{2+} + e^- \\
   \text{Ag}(s) + \text{Cl}^- & \leftrightarrow \text{AgCl}(s) + e^- 
   \end{align*}
   \]
   
   - e\(^{-}\) is taken up by electrode into electrical circuit
d.) **Liquid junctions** –

interface between two solutions with different components or concentrations

Small potentials may develop at junction that affect overall cell potential
Cells without liquid junction

If the voltmeter were removed and replaced by a wire, silver would behave as the cathode. The reaction at the cathode would be

\[
\text{AgCl(s)} + e^- \rightarrow \text{Ag}^+(aq) + \text{Cl}^- (aq)
\]

Under discharge, hydrogen is consumed at the platinum anode:

\[
\text{H}_2 (q) \rightarrow 2\text{H}^+ (aq) + 2e^-
\]

Overall:

\[
2\text{AgCl (s)} + \text{H}_2(g) \rightarrow 2\text{Ag(s)} + 2\text{H}^+ + 2\text{Cl}^-
\]

Note that in this case the inert platinum electrode plays no direct role in the reaction but serves only as a surface where electron transfer can occur.

you cannot tell whether a given electrode will be a cathode or an anode unless you know whether the cell is galvanic under discharge or electrolytic.
Solution Structure: Electrical double layer

Electrochemical measurements are made on heterogeneous systems and an electrode can only donate or accept electrons from a species that is present in a layer of solution that is immediately adjacent to the electrode. Thus, this layer may have composition that differs significantly from that of the bulk of the solution. The surface of the metal electrode is shown as having an excess of positive charge as a consequence of an applied positive potential.

The charged solution layer consists of two parts:
1. tightly bound inner layer (potential decreases linearly with distance)
2. loosely bound outer layer (the decrease is exponential.)

This assemblage of charge at the electrode surface and in the solution adjacent to the surface is termed an electrical double layer.
Faradaic and Nonfaradaic Currents

Two types of processes can conduct currents across an electrode/solution interface.

i.) Faradic
   ① transfer of e\textsuperscript{-} to/from electrode by redox reactions
   ② governed by Faraday’s Law
   - amount of current is proportional to amount of species oxidized or reduced

ii.) Non-Faradic Current
   ① due to processes other than redox reactions at electrodes
      ② example – charging current
      - when first apply potential to electrode, get redistribution of ions near its surface to counter charge on electrode
      \[ \text{movement of ions} = \text{current} \]
      - as system approaches equilibrium \( \rightarrow \) get decrease in ion movement and current
A faradaic current requires continuous mass transfer of reactive species from the bulk of the solution to the electrode surface. Three mechanisms bring about this mass transfer:

**Convection** involves mechanical motion of the solution as a result of stirring or the flow of the solution past the surface of the electrode.

**Migration** is the movement of ions through the solution brought about by electrostatic attraction between the ions and the charged electrode.

**Diffusion** is the motion of species brought about by a concentration gradient.
Representation of Cells: by convention start with anode on left

Zn|ZnSO₄\(a_{\text{Zn}^{2+}} = 0.0100\)||CuSO₄\(a_{\text{Cu}^{2+}} = 0.0100\)|Cu

Phase boundary
Electrode/solution interface

anode → oxidation
Solution in contact with anode & its concentration

2 liquid junctions due to salt bridge
Solution in contact with cathode & its concentration

cathode → reduction

Volmeter
1.100 V

Salt bridge
Saturated KCl solution

Zn electrode
0.0100 M ZnSO₄ solution
Zn(s) = Zn²⁺(aq) + 2e⁻
\(a_{\text{Zn}^{2+}} = 0.010\)
Anode

Cu electrode
0.0100 M CuSO₄ solution
Cu²⁺(aq) + 2e⁻ = Cu(s)
\(a_{\text{Cu}^{2+}} = 0.010\)
Cathode
for convenience, represent overall reaction in cell as two ½ reactions
   i. one at anode & other at cathode
   ii. each ½ reaction has certain potential associated with it
   iii. by convention, write both ½ reactions as reduction:
           \[
           \begin{align*}
           \text{Cu}^{2+} + 2e^- & \leftrightarrow \text{Cu(s)} \quad (E_{\text{cathode}}) \\
           \text{Zn}^{2+} + 2e^- & \leftrightarrow \text{Zn(s)} \quad (-E_{\text{anode}})
           \end{align*}
           \]
   iv. potential of cell is then defined as:
           \[
           E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}
           \]
2.) *Problem* – can not measure potential of just one electrode.
   i. need to compare to another electrode
   ii. determine potential of all $\frac{1}{2}$ cell reactions vs. a *common* reference electrode
   iii. reference electrode – *standard hydrogen electrode* (SHE)

$$\text{Pt, H}_2(p \text{ atm}) | \text{H}^+(a_{\text{H}^+} = x)$$
$$2\text{H}^+ + 2e^- \leftrightarrow \text{H}_2(\text{g})$$

Stream of $\text{H}_2$ keeps surface at electrode saturated w/$\text{H}_2(\text{g})$

*note*: potential affected by pH, $[\text{H}^+]$, used as an early pH indicator, also dependent on $P$
By convention, $E_{\text{SHE}} = 0\text{V}$ at $[\text{H}^+] = 1\text{M}$, $P_{\text{H}_2} = 1\text{ atm}$ and at all temperatures.

Potentials of other electrodes are compared to SHE using electrode in question as cathode and SHE as anode:

$$M^{n+} + ne^- \leftrightarrow M(\text{s})$$

By definition:

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$
$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{SHE}}$$
$$E_{\text{cell}} = E_{\text{cathode}} - 0$$
$$E_{\text{cell}} = E_{\text{cathode}}$$
Standard Electrode Potential (E°) – measured $E_{cell}$ when all species in solution or gas has an activity of 1.00

Activity (a) – proportional to molar concentration

$$a_x = \gamma_x[X]$$

where:

$\gamma_x$ is the activity coefficient of solute $X$

$[X]$ is the molar concentration of solute $X$

If $E^o$ is “+”, it indicates that the reaction:

$$M^{n+} + n/2H_2(g) \leftrightarrow M(s) + nH^+$$

is favored or spontaneous.

$M^{n+}$ is readily reduced by $H_2(g) \therefore M^{n+}$ is better $e^-$ acceptor or oxidizing agent.

If $E^o$ is “-”, it indicates that the reaction is not favored or spontaneous and requires energy to proceed

$M(s)$ is readily oxidized by $H^+ \therefore M(s)$ is better $e^-$ donor or reducing agent.
<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E^0$ at $25^\circ$C, V</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cl}_2(g) + 2e^- \rightleftharpoons 2\text{Cl}_2$</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>$\text{Br}_2(aq) + 2e^- \rightleftharpoons 2\text{Br}_2$</td>
<td>+1.087</td>
</tr>
<tr>
<td>$\text{Br}_2(l) + 2e^- \rightleftharpoons 2\text{Br}_2$</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>$\text{Hg}_2\text{Cl}_2(s) + 2e^- \rightleftharpoons 2\text{Hg}(l) + 2\text{Cl}_2$</td>
<td>+0.268</td>
</tr>
<tr>
<td>$\text{AgCl}(s) + e^- \rightleftharpoons \text{Ag}(s) + \text{Cl}_2$</td>
<td>+0.222</td>
</tr>
<tr>
<td>$\text{Ag(S}_2\text{O}_3)_2^{3-} + e^- \rightleftharpoons \text{Ag}(s) + 2\text{S}_2\text{O}_3^{2-}$</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>$\text{AgI}(s) + e^- \rightleftharpoons \text{Ag}(s) + \text{I}_2$</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>
As $E^0$ increases $\rightarrow$ oxidizing ability of $\frac{1}{2}$ cell reaction increases

<table>
<thead>
<tr>
<th>Reaction at Interface</th>
<th>Half-cell Potential ($E^0$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}^{3+} + 3e^- \rightarrow \text{Al}$</td>
<td>$-1.706 \text{ V}$</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}$</td>
<td>$-0.763 \text{ V}$</td>
</tr>
<tr>
<td>$\text{Cr}^{3+} + 3e^- \rightarrow \text{Cr}$</td>
<td>$-0.744 \text{ V}$</td>
</tr>
<tr>
<td>$\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe}$</td>
<td>$-0.409 \text{ V}$</td>
</tr>
<tr>
<td>$\text{Cd}^{2+} + 2e^- \rightarrow \text{Cd}$</td>
<td>$-0.401 \text{ V}$</td>
</tr>
<tr>
<td>$\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}$</td>
<td>$-0.230 \text{ V}$</td>
</tr>
<tr>
<td>$\text{Pb}^{2+} + 2e^- \rightarrow \text{Pb}$</td>
<td>$-0.126 \text{ V}$</td>
</tr>
<tr>
<td>$2\text{H}^+ + 2e^- \rightarrow \text{H}_2$</td>
<td>$0.00 \text{ V}$</td>
</tr>
<tr>
<td>$\text{AgCl} + e^- \rightarrow \text{Ag} + \text{Cl}^-$</td>
<td>$+0.223 \text{ V}$</td>
</tr>
<tr>
<td>$\text{Hg}_2\text{Cl}_2 + 2e^- \rightarrow 2\text{Hg} + 2\text{Cl}^-$</td>
<td>$+0.268 \text{ V}$</td>
</tr>
<tr>
<td>$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$</td>
<td>$+0.340 \text{ V}$</td>
</tr>
<tr>
<td>$\text{Ag}^+ + e^- \rightarrow \text{Ag}$</td>
<td>$+0.799 \text{ V}$</td>
</tr>
<tr>
<td>$\text{Au}^+ + e^- \rightarrow \text{Au}$</td>
<td>$+1.680 \text{ V}$</td>
</tr>
</tbody>
</table>
Nernst Equation

Values of $E_{\text{electrode}}$ can also be calculated at other concentrations (activities) of species for $\frac{1}{2}$ reaction:

$$\text{pP + qQ + ... + ne}^- \leftrightarrow \text{rR + sS + ...}$$

$$E_{\text{electrode}} = E^0 - \frac{RT}{nF} \ln \left( \frac{a_R^r a_S^s \ldots}{a_P^p a_Q^q \ldots} \right)$$

where:

- $R =$ ideal gas law constant ($8.316 \text{ J mol}^{-1} \text{ K}^{-1}$)
- $T =$ absolute temperature (K)
- $n =$ number of electrons in process
- $F =$ Faraday’s constant ($96487 \text{ C mol}^{-1}$)
- $a =$ activities of each species ($\gamma[X]$)
  - in solution at time of measurement
  - not necessarily at equilibrium
At room Temperature:

\[
\frac{RT}{nF} = \frac{2.5693 \times 10^{-2}}{n} \text{ V}
\]

Also, using \( \log_{10} \):

\[
E_{\text{electrode}} = E^0 - \frac{0.0592}{n} \log \left( \frac{(a_R)^r(a_S)^s \ldots}{(a_P)^p(a_Q)^q \ldots} \right)
\]

If know \( E^0 \), allows \( E_{\text{electrode}} \) to be calculated under non-standard conditions.

Note: If all activity values = 1, \( E_{\text{electrode}} = E^0 \)

Once have \( E_{\text{cathode}} \) & \( -E_{\text{anode}} \) by above procedure, can also get \( E_{\text{cell}} \):

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

may need to also include junction potential, etc., but good first approximation
Activity Coefficients
- experimental determination of individual activity coefficients appears to be impossible
- can determine mean activity coefficient ($\gamma_{\langle \rangle}$):

$$ \text{electrolyte } A_m B_n \rightarrow \gamma_{\langle \rangle} = (\gamma_A^m \gamma_B^n)^{1/(M+n)} $$

Debye-Huckel Equation

$$ - \log \gamma_A = \frac{0.509 Z_A^2 \sqrt{\mu}}{1 + 3.28 \alpha_A \sqrt{\mu}} $$

where:
- $Z_A$ = charge on the species A
- $\mu$ = ionic strength of solution
- $\alpha_A$ = the effective diameter of the hydrated ion

<table>
<thead>
<tr>
<th>Ion</th>
<th>$\alpha_x$ nm</th>
<th>0.001</th>
<th>0.005</th>
<th>0.01</th>
<th>0.05</th>
<th>0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_3O^+$</td>
<td>0.9</td>
<td>0.967</td>
<td>0.933</td>
<td>0.914</td>
<td>0.86</td>
<td>0.83</td>
</tr>
<tr>
<td>Li$^+$</td>
<td>0.6</td>
<td>0.965</td>
<td>0.929</td>
<td>0.907</td>
<td>0.84</td>
<td>0.80</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>0.4-0.45</td>
<td>0.964</td>
<td>0.928</td>
<td>0.902</td>
<td>0.82</td>
<td>0.78</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>0.3</td>
<td>0.964</td>
<td>0.925</td>
<td>0.899</td>
<td>0.80</td>
<td>0.76</td>
</tr>
</tbody>
</table>

Note: At ionic strengths > 0.1, Debye-Huckle Equation fails
**An Example:**

Calculate $E_{\text{cell}}$ for the Cell:

\[ \text{Pt} | \text{H}_2 (1.00 \text{ atm}) | \text{HCl} \ (3.215 \times 10^{-3} \text{M}), \text{AgCl} \ (\text{satd.}) | \text{Ag} \]

$\frac{1}{2}$ cell reactions:

\[ \text{AgCl} (s) + e^- \leftrightarrow \text{Ag} (s) + \text{Cl}^- \quad E^0 = 0.222 \text{ V} \]

\[ \text{H}^+ + e^- \leftrightarrow \frac{1}{2} \text{H}_2 (g) \quad E^0 = 0.00 \text{ V} \]

$E^0_{\text{AgCl/Ag}} > E^0_{\text{H}^+/\text{H}_2}$, so net reaction is spontaneous:

\[ \text{AgCl} (s) + \frac{1}{2} \text{H}_2 \leftrightarrow \text{Ag} (s) + \text{H}^+ + \text{Cl}^- \]

Actual Potentials:

**Cathode**

\[ E_{\text{cathode}} = E^0_{\text{AgCl}} - (0.0592/1) \log a_{\text{Cl}^-} \quad \rightarrow \text{since satd. solids, activity of AgCl and Ag = 1.} \]

\[ E_{\text{cathode}} = E^0_{\text{AgCl}} - 0.0592 \log y_{\text{Cl}^-} \cdot \text{[Cl}^-\text{]} \]

\[ E_{\text{cathode}} = 0.222 \text{ V} - 0.0592 \log (0.939)(3.215 \times 10^{-3} \text{M}) \]

\[ 0.939 \rightarrow \text{Debye-Huckle equation } \mu = 3.215 \times 10^{-3} \text{ Cl}^- \]

\[ E_{\text{cathode}} = 0.371 \text{ V} \]
½ cell reactions:

\[
\begin{align*}
\text{AgCl(s) + e}^- & \leftrightarrow \text{Ag(s) + Cl}^- & E^0 = 0.222 \text{ V} \\
\text{H}^+ + e^- & \leftrightarrow \frac{1}{2} \text{H}_2(g) & E^0 = 0.00 \text{ V} \\
\text{AgCl(s) + } \frac{1}{2} \text{H}_2 & \leftrightarrow \text{Ag(s) + H}^+ + \text{Cl}^- \\
\end{align*}
\]

Actual Potentials:

**Anode**

\[
E_{\text{anode}} = E^0_{\text{H}^+/\text{H}_2} - (0.0592/1) \log (a_{\text{H}^+})/(P^{1/2}_{\text{H}_2})
\]

\[
E_{\text{anode}} = E^0_{\text{H}^+/\text{H}_2} - 0.0592 \log (\gamma_{\text{H}^+}[\text{HCl}])/(P^{1/2}_{\text{H}_2})
\]

\[
E_{\text{anode}} = 0.00 \text{ V} - 0.0592 \log (0.945)(3.215 \times 10^{-3} \text{M})/(1 \text{ atm})^{1/2}
\]

0.945 \rightarrow \text{Debye-Huckle equation} \quad \mu = 3.215 \times 10^{-3} \text{H}^+

\[
E_{\text{anode}} = 0.149 \text{ V}
\]

\[
\therefore \quad E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = 0.371 \text{ V} - 0.149 \text{ V} = 0.222 \text{ V}
\]
6.) Limitations in the Use of Standard Electrode Potentials ($E^0$):

a.) $E^0$ based on unit activities not concentrations

- activity = concentration only in dilute solutions
- at higher concentrations need to determine and use activity

$$a_x = \gamma_x [X]$$

- example:

$$\text{Fe}^{3+} + e^- \leftrightarrow \text{Fe}^{2+} \quad E^0 = +0.771 \text{ V}$$

but $E$ at 1M is +0.732 V, since $\gamma < 1$

- problem if $\gamma$ not known from calculations or previous experimental studies

b.) Side Reactions can Affect $E^0$ Apparent:

- example:

$$\text{Fe}^{3+} + e^- \leftrightarrow \text{Fe}^{2+} \quad E = +0.73 \text{ V in 1M HClO}_4$$

$$\text{Fe}^{3+} + e^- \leftrightarrow \text{Fe}^{2+} \quad E = +0.70 \text{ V in 1M HCl}$$

$$\text{Fe}^{3+} + e^- \leftrightarrow \text{Fe}^{2+} \quad E = +0.60 \text{ V in 1M H}_3\text{PO}_4$$

- reason: $\text{Fe}^{2+}$ & $\text{Fe}^{3+}$ form different complexes with Cl$^-$ & PO$_4$$^-$ that affects net activity of $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ in solution
7.) Formal Potential ($E^f$ or $E^o'$):
- used to compensate for problems with $E^o$ in using activity and with side-reactions
- based on conditions of 1M concentration with all species being specified
e.g. HCl vs. HClO$_4$ as acid
- gives better agreement than $E^o$ with experimental data and Nernst Equation
  \[ 2 \text{ conditions need to be similar to conditions where } E^o' \text{ was measured} \]

8.) Reaction Rates:
- some $E^o$ $\frac{1}{2}$ reactions listed in tables have been determined by calculations from equilibrium measurements rather than actual measurements of the $\frac{1}{2}$ cell in an electrode system.
  \[ \text{e.g. } 2\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{H}_2\text{C}_2\text{O}_4 \quad E^0 = -0.49 \text{ V} \]
- problem
  \[ 2 \text{ reaction is slow and difficult to see in practice} \]
  \[ 2 \text{ thermodynamics vs. kinetics} \]
  \[ 2 \text{ no suitable electrode} \]
- potentially useful for computational purposes
9.) Liquid Junction Potential

- potential that develops whenever two electrolytes of different ionic composition come into contact
- due to the unequal distribution of cations & anions across a boundary as a result of the differences in rates at which ions migrate.

Both $H^+$ & $Cl^-$ move from high to low concentration (entropy)

$H^+$ smaller and more mobile relative to $Cl^-$, moves more quickly

Results in separation of “+” and “-” charges and creation of potential

*Note:* Equilibrium condition soon develops
- junction potential can be $\geq 30 \text{ mV}$
  ② for simple system can calculate if know mobility and concentration of all ions present
- can decrease the junction potential by using salt bridge containing concentrated electrolyte
  ② best if mobility of ions are ~ equal
  ② 4 M KCl or KNO$_3$
  ② decrease junction potential to $\leq$ few mV
10.) *Currents in Electrochemical Cells*

a) Ohm’s Law

\[ E = IR \]

where:

- \( E \) = potential (V, voltage)
- \( I \) = current (amps)
- \( R \) = resistance (ohms)

> *R depends on concentration and types of ions in solution* <

\[ I = \frac{E}{R_1 + R_2} \]
11.) **Effect of Current on Cell Potential**

- potentials listed as \( E^0 \) or \( E^{0'} \) in Tables are **Thermodynamic values**
  - \( \Delta \) at equilibrium, no current
- in practice, some current is always present.
- current causes
  - \( \Delta \) decrease in measured potential (E) for galvanic cell
  - \( \Delta \) increase in potential (E) needed to drive electrolytic cell

**Two Main Sources of Current Effects on Cell Potential:**

i.) **Ohmic Potential (IR drop)**

- flow of ions (current) through solution (resistance, \( R \)) gives potential across cell according to Ohm’s law

\[
E = IR
\]

- need to subtract from \( E_{cell} \) calculation to get “true” potential of the cell

\[
E_{cell} = E_{cathode} - E_{anode} - IR
\]
ii.) **Polarization Effects**
- many electrochemical methods use current vs. potential curves

Note: at high or low cell potential, get less “+” or “-” current than expected.
- due to *polarization*
  ① solution or reaction can not keep up with changes in potential of system
  ② limits the rate of the overall reaction
Types of Polarization

1) Slow Mass Transfer = Concentration Polarization
   
   - mass transfer due to:
     - diffusion → concentration gradient
     - migration → ions move in potential
     - convection → mechanical stirring

2) Slow Intermediate Reactions = Reaction Polarization

3) Slow Transfer of Electron Between Electrode and Species = Charge-Transfer Polarization

Any Combination of These Processes Can Be Present.
**Overvoltage or Overpotential ($\eta$)**

- degree of polarization of an electrode
- difference between actual electrode potential ($E$) and equilibrium potential ($E_{eq}$)

\[ \eta = E - E_{eq} \]

where

\[ E < E_{eq} \]

- polarization *always* reduces the electrode potential
- $\eta$ is *always* negative

**Overvoltage is sometimes useful:**

- high overvoltage associated with the formation of $H_2$ & $O_2$ from $H_2O$
- high $\eta$ means takes much higher $E$ than $E^0$ to occur on many electrodes
- can deposit metals without $H_2$ formation and interfering with electrodeposition process
Example 17: Calculate $E^\circ$ for the process

$$\text{Ni(CN)}_4^{2-} + 2e^- \rightleftharpoons \text{Ni(s)} + 4\text{CN}^-$$

given the formation constant ($K_f$) for the complex is $1.0 \times 10^{22}$