Chapter 2 – Thermodynamics and Potentials

Thermodynamics encompass systems at equilibrium!

- **Chemical Reversibility** = chemical reactions associated with the electrochemical reaction are reversible.
  
  \[ \text{Pt/H}_2/\text{H}^+ , \text{Cl}^-/\text{AgCl}/\text{Ag} \text{ (standard states)} \]
  
  \[ E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = E_c - E_a = 0.222 - 0.000 = 0.222 \text{ V} \]
  
  \[ \text{H}_2 + 2\text{AgCl} \leftrightarrow 2\text{Ag} + 2\text{H}^+ + 2\text{Cl}^- \]

- **Thermodynamic Reversibility** = Infinitesimal driving force causes the reaction to move forward/reverse direction. Essentially at equilibrium.

- **Practical Reversibility** = Actual processes occur at finite rates, therefore, they cannot proceed at true equilibrium. However, processes can be carried out in a manner in which thermodynamic considerations apply.

  \[ E = E^0 + (2.303RT/nF) \log[\text{Ox}]/[\text{Red}] \]

Link between E and concs. at surface. (removal of weight/slow or fast)
Thermodynamic Quantities

- \( \Delta G_{\text{rxn}} = -nF E_{\text{rxn}} \) \hspace{1cm} \( \Delta G^o_{\text{rxn}} = -nF E^o_{\text{rxn}} \)

- \( \Delta S = -(\frac{\partial \Delta G}{\partial T})_p = nF(\frac{\partial E_{\text{rxn}}}{\partial T})_p \)

- \( \Delta H = \Delta G + T \Delta S = nF[T(\frac{\partial E_{\text{rxn}}}{\partial T})_p - E_{\text{rxn}}] \)

- \( RT \ln K_{\text{rxn}} = -\Delta G^o = nF E^o_{\text{rxn}} \)

- emf relates to the direction of the reaction. Reduction potential (O/R couple) vs. emf for the reduction or oxidation reaction.
Formal Potentials

- Standard conditions for $E^o$ (298 K, pH = 0, $a = 1$)

- Non-standard conditions or conditions where the activities of Ox and Red are affected by the medium, then formal potentials are used, $E^{o'}$.

- The formal potential incorporates the standard potential and some activity coefficients.

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

$$E^{o'} = E^o + \frac{2.303RT}{nF}\log \frac{\gamma_{ox}}{\gamma_{red}}$$
Reference Electrodes

- Reversible and obeys the Nernst Eq. (chemical and echem).
- Constant E with time.
- Returns to original potential with passage of small currents.
- Exhibits little hysteresis with temperature cycling.

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

1 M NaCl or KCl

AgCl coated on Ag

Porous glass frit

AgCl(s) + e⁻ → Ag(s) + Cl⁻(aq)

$E_{ref} = E^o + (0.059/1) \log \frac{1}{[Cl^-]}$

$E_{ref} = 0.222 \, V \text{ vs. NHE}$

if $[Cl^-] = 1 \, M$

Quasi-reference electrodes are sometimes used, Pt or Ag
Electrode Potential Measurement

Two electrodes (two interfaces) are required to make a potential measurement!

Figure 2.2.3 Potential profile through the system shown in Figure 2.2.2. Distance is measured radially from the center of the metallic sphere.
Interfacial Potentials
Changes in potential of a conducting phase can be affected by altering the charge distribution on or around the phase.

If phase undergoes a change in excess charge, the excess charge will be distributed over the entire boundary of the phase.
Measurement of Potential Differences

- Electrons can be pumped into or out of a metal electrode using a power supply.

- $\Delta \phi$ controls the relative energies of charged species on either side of the interface. $\Delta \phi$ controls relative electron affinities of the two phases – the direction of the reaction.

Cu/Zn/Zn$^{+2}$, Cl$^-$/AgCl/Ag/Cu$'$

- $E_{cell}$ is sum of several interfacial potentials and none can be measured independently.

- Maintain constant interfacial potentials at all interfaces then change in $E$ must be due to changes at electrode-solution interface (Zn/electrolyte).
Electrochemical Potentials
Junction Potentials

- Zn$^{+2}$ energy state depends on local chemical and electrical environment.

\[ \text{Cu/Zn/Zn}^{+2}/\text{Cu}^{+2}/\text{Cu'} \]

\[ E_{\text{cell}} = (\phi^{\text{Cu'}} - \phi^\beta) - (\phi^{\text{Cu}} - \phi^\alpha) + (\phi^\beta - \phi^\alpha) \]

\( (\phi^\beta - \phi^\alpha) \) is the diffusion potential or junction potential between two solutions.

1. Two solutions of same electrolyte at different concentrations.
2. Two solutions of same concentration with different electrolytes having a common ion.
3. Two solutions not satisfying #1 or 2.
Junction Potentials

\[ \Sigma t_i = 1 \]

Transference number – fraction of current carried by ion

\[ t_+ + t_- = 1 \]

\[ L = \kappa A/l \]

Conductance (ohm\(^{-1}\))

\[ \kappa = F \Sigma_i |z_i| u_i C_i \]

Conductivity (ohm\(^{-1}\) cm\(^{-1}\))

\[ t_i = \frac{|z_i| u_i C_i}{\Sigma |z_j| u_j C_j} \]

\[ u = \frac{v \text{ (cm/s)}}{E \text{ (V/cm)}} \{\text{cm}^2/\text{V-s}\} \]
Junction Potentials

\[ E_j = (\varphi^\beta - \varphi^\alpha) = (t_+ - t_-)(RT/F)\ln(a_1/a_2) \]

Type 1 1:1 electrolyte junction

\[ a(\text{H}^+) = a(\text{Cl}^-) = a_1 \quad a(\text{H}^+) = a(\text{Cl}^-) = a_2 \]

For \( a_1 = 0.01 \text{ M} \) and \( a_2 = 0.1 \text{ M} \) and \( t(\text{H}^+) = 0.83 \) and \( t(\text{Cl}^-) = 0.17 \), \( E_j = -39.1 \text{ mV} \)

\[ E_j = (\varphi^\beta - \varphi^\alpha) = -(RT/F)\sum_i (t_i/z_i) d\ln(a_i) \]

General expression for \( E_j \).