

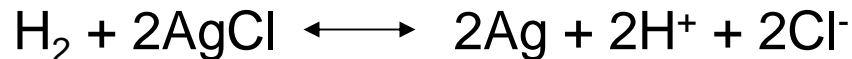
Chapter 2 – Thermodynamics and Potentials

Thermodynamics encompass systems at equilibrium!

- **Chemical Reversibility** = chemical reactions associated with the electrochemical reaction are reversible.

Pt/H₂/H⁺, Cl⁻/AgCl/Ag (standard states)

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = E_{\text{c}} - E_{\text{a}} = 0.222 - 0.000 = 0.222 \text{ V}$$



- **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

- $\Delta G_{\text{rxn}} = -nFE_{\text{rxn}}$ $\Delta G^{\circ}_{\text{rxn}} = -nFE^{\circ}_{\text{rxn}}$
- $\Delta S = -(\partial\Delta G/\partial T)_p = nF(\partial E_{\text{rxn}}/\partial T)_p$
- $\Delta H = \Delta G + T\Delta S = nF[T(\partial E_{\text{rxn}}/\partial T)_p - E_{\text{rxn}}]$
- $RT (\ln K_{\text{rxn}}) = -\Delta G^{\circ} = nFE^{\circ}_{\text{rxn}}$
- 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° (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, $E^{\circ'}$.
- The formal potential incorporates the standard potential and some activity coefficients.

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

$$E^{\circ'} = E^\circ + (2.303RT/nF)\log \gamma_{\text{ox}}/\gamma_{\text{red}}$$

Reference Electrodes

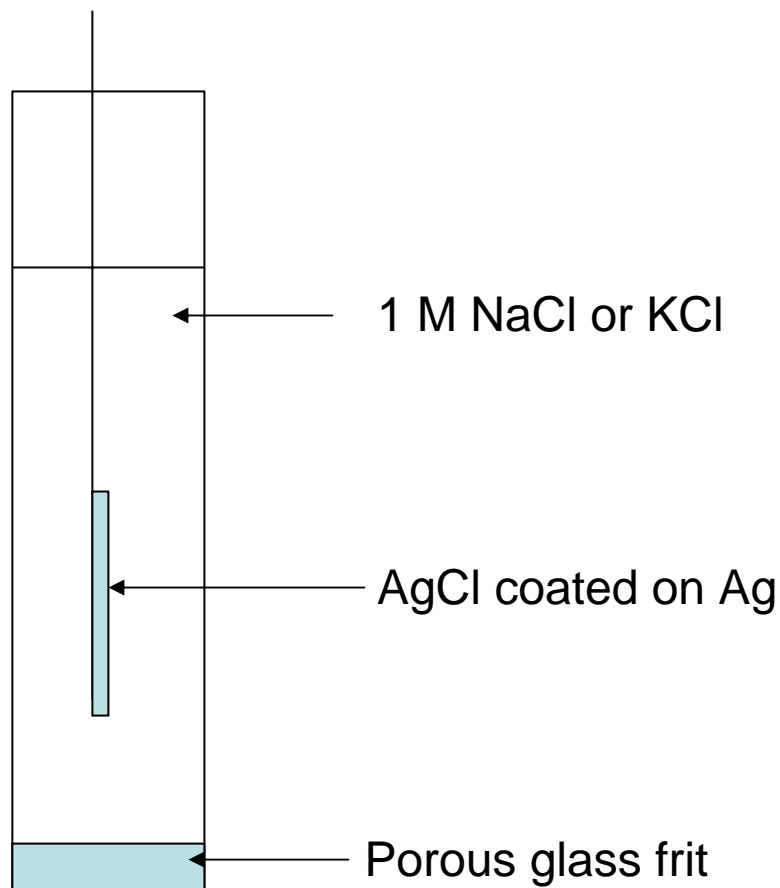
- Reversible and obeys the Nernst Eq. (chemical and echem).
- Constant E with time.
- Returns to original potential with passage of small currents.
- Exhibits little hysteresis with temperature cycling.

| | | | | |
|--------------------------------------|------------------------|------------------------|---------------------------|------------------------------|
| $E^0(\text{Zn}^{2+}/\text{Zn})$ | -0.763 | -1.00 | 3.7 | -3.7 |
| NHE | 0 | -0.242 | 4.5 | -4.5 |
| SCE | 0.242 | 0 | 4.7 | -4.7 |
| $E^0(\text{Fe}^{3+}/\text{Fe}^{2+})$ | 0.77 | 0.53 | 5.3 | -5.3 |
| | E vs. NHE (volts) | E vs. SCE (volts) | E vs. vacuum (volts) | E_F (Fermi energy) (eV) |

Figure 2.1.1 Relationship between potentials on the NHE, SCE, and “absolute” scales. The potential on the absolute scale is the electrical work required to bring a unit positive test charge into the conducting phase of the electrode from a point *in vacuo* just outside the system (see Section 2.2.5). At right is the Fermi energy corresponding to each of the indicated potentials. The Fermi energy is the electrochemical potential of electrons on the electrode (see Section 2.2.4).

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

Reference Electrodes



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

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

if $[\text{Cl}^-] = 1 \text{ M}$

Quasi-reference electrodes are sometimes used, Pt or Ag

Electrode Potential Measurement

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

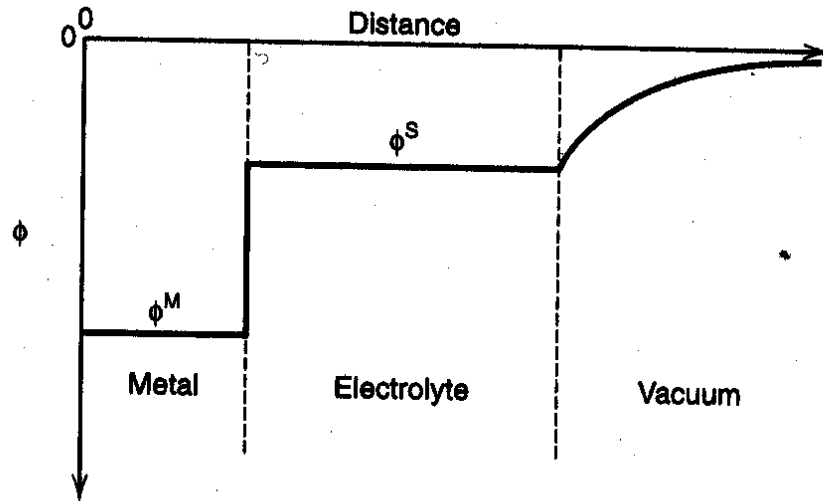
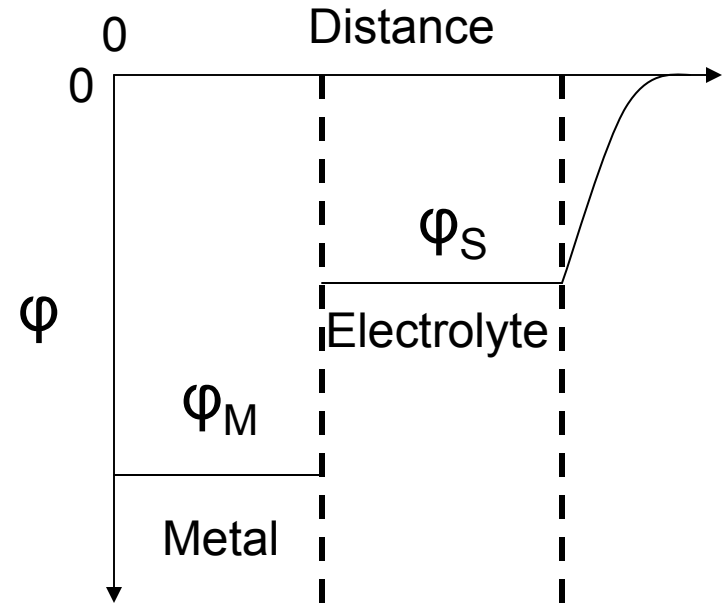
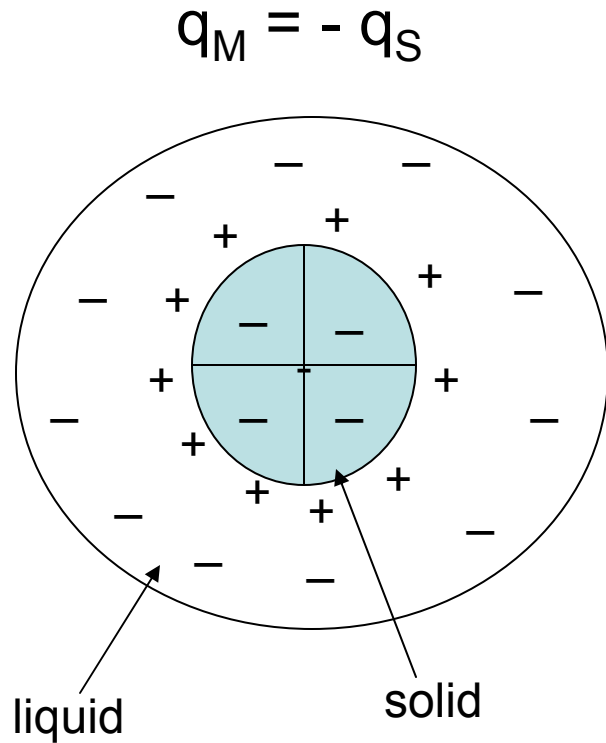


Figure 2.2.3 Potential profile through the system shown in Figure 2.2.2. Distance is measured radially from the center of the metallic sphere.

Interfacial Potentials

Interactions Between Phases



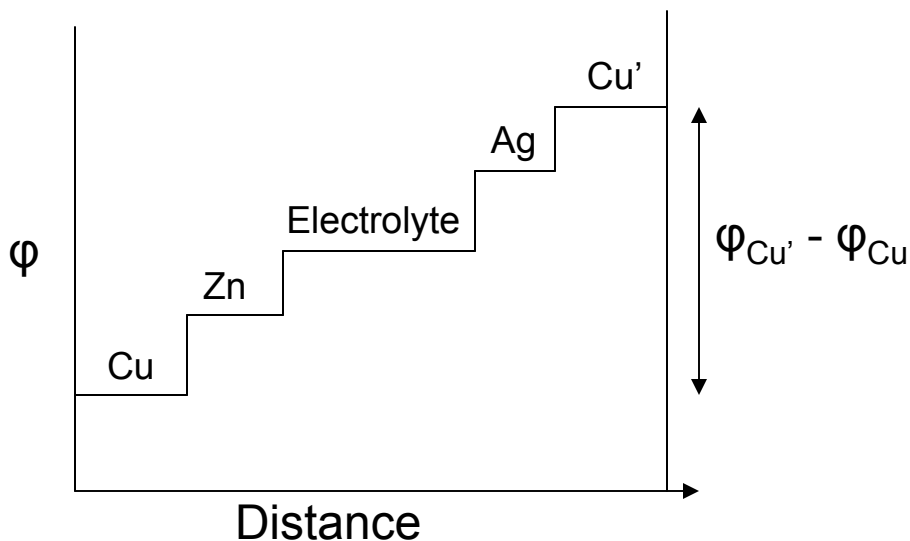
$\phi_M - \phi_S =$ interfacial potential difference
{depends on charge imbalance and
size of interface}

- 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/Zn²⁺, Cl⁻/AgCl/Ag/Cu'

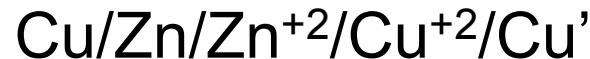


- E_{cell} is sum of several interfacial potentials and none can be measured independently.
- Maintain constant interfacial potentials at all interfaces then change in E must be due to changes at electrode-solution interface (Zn/electrolyte).

Electrochemical Potentials

Junction Potentials

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



$$E_{\text{cell}} = (\varphi^{\text{Cu}'} - \varphi^{\beta}) - (\varphi^{\text{Cu}} - \varphi^{\alpha}) + (\varphi^{\beta} - \varphi^{\alpha})$$

$(\varphi^{\beta} - \varphi^{\alpha})$ 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

$$\sum_i t_i = 1$$

Transference number – fraction of current carried by ion

$$t_+ + t_- = 1$$

$$L = \kappa A/l$$

Conductance (ohm^{-1})

$$\kappa = F \sum_i |z_i| u_i C_i$$

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

$$t_i = \frac{|z_i| u_i C_i}{\sum_j |z_j| u_j C_j}$$

$$u = \frac{v \text{ (cm/s)}}{E \text{ (V/cm)}} \quad \{\text{cm}^2/\text{V-s}\}$$

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

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

General expression for E_j .