\( E^o \) and Thermodynamics

- \( E^o \) is related to \( \Delta G^o \), the free energy change for the reaction.
- \( \Delta G^o \) proportional to \(-nE^o\)

\[
\Delta G^o = -nFE^o
\]

where \( F \) = Faraday constant = 9.6485 x 10^4 J/V mol of e^-
(or 9.6485 x 10^4 coulombs/mol)
and \( n \) is the number of moles of electrons transferred

For a product-favored reaction
Reactants \( \longrightarrow \) Products
\( \Delta G^o < 0 \) and so \( E^o > 0 \)
\( E^o \) is positive

For a reactant-favored reaction
Reactants \( \longleftarrow \) Products
\( \Delta G^o > 0 \) and so \( E^o < 0 \)
\( E^o \) is negative

\( E^o \) and \( \Delta G^o \)

\[ \Delta G^o = -nFE^o \]

For a product-favored reaction
Reactants \( \longrightarrow \) Products
\( \Delta G^o < 0 \) and so \( E^o > 0 \)
\( E^o \) is positive

For a reactant-favored reaction
Reactants \( \longleftarrow \) Products
\( \Delta G^o > 0 \) and so \( E^o < 0 \)
\( E^o \) is negative

\( E^o \) and Thermodynamics

- \( E^o \) is temperature dependent.
- \( E^o \) is related to standard free energy change.

\[ E^o = \Delta G^o \text{ (at standard conditions)} \]

\( E^o \) used to find \( K \) and \( K \) used to find \( E^o \)

\( E^o \) and \( \Delta G^o \)

\[
\Delta G^o = -nFE^o
\]

Nernst Equation

\[
E = E^o - \frac{RT}{nF} \ln \frac{[\text{Products}]}{[\text{Reactants}]}
\]

- \( E = \) potential under nonstandard conditions
- \( n = \) no. of electrons exchanged
- If \([P]\) and \([R]\) = 1 mol/L, then \( E = E^o \)
- If \([R] > [P]\), then \( E \) is \( \underline{\text{lower than}} \) \( E^o \)
- If \([R] < [P]\), then \( E \) is \( \underline{\text{higher than}} \) \( E^o \)

Using the Nernst Equation

- What is the potential of a cell involving a Cd^{2+}(aq)/Cd(s) half-cell and a Ni^{2+}(aq)/Ni(s) half-cell when \([Cd^{2+}] = 0.050 \text{ M and } [Ni^{2+}] = 0.010 \text{ M}?)
- \( \Delta G^o \) = \( \Delta G^o \) (at standard conditions)

Using the Nernst Equation

- \( E^o \) used to find K and K used to find \( E^o \)
- \( E^o = (0.0592/n) \log K \)
- \( E^o \) used to find K and K used to find \( E^o \)
Using the Nernst Equation: Calculate $K$

- Calc. $K_y$ for AgCl(s) $\rightleftharpoons$ Ag⁺(aq) + Cl⁻(aq)
- Set up cell with AgCl/Ag electrode and Ag⁺/Ag electrode
- Anode: Ag(s) $\rightarrow$ Ag⁺(aq) + e⁻(aq)
- $E^- = E^-_{\text{anode}} - E^-_{\text{cathode}}$
- $E^- = (0.222 \text{ V}) - (+0.799 \text{ V}) = -0.577 \text{ V}$
- Log $K_y = (1) (-0.577 \text{ V})/0.0592 \text{ V} = -9.75$
- $K_y = 1.8 \times 10^{-9}$

Using the Nernst Equation: Concentration Cells

- In a concentration cell there is no net oxidation or reduction, only a change in concentration.
- Now $E^\prime = 0$
- For example: Fe(1, s) + Fe²⁺(2, 0.010 M) $\rightleftharpoons$ Fe⁺(1, 0.0050 M) + Fe(2, s)
- Anode: Fe(s) $\rightarrow$ Fe⁺(aq) + 2e⁻ E$^\prime$ = -0.44 V
- $E^-_{\text{cell}} = 0.00 \text{ V}$
- $E^\prime$ = 0 - (0.0592 V/2) log (0.0050/0.010) = 0.009 V

Latimer diagrams

- In a Latimer diagram for an element, the numerical value for $E^\prime$ (V) is written over a horizontal line connecting species in different oxidation states.

\[
\begin{array}{ccc}
-0.04 V & 0.771 V & -0.44 V \\
\text{Fe³⁺} & \text{Fe²⁺} & \text{Fe} \\
\end{array}
\]

How do we derive the potential for Fe²⁺ + 3e⁻ $\rightarrow$ Fe(s)?

Frost Diagrams

- Frost diagram is a plot of $NE^\prime$ versus oxidation number (N) for the couple X + N⁻ $\rightarrow$ X⁻ N$^\prime$
- Essentially a free energy plot because $\Delta G/F = NE^\prime$
- The most stable oxidation state lies lowest in the diagram.

Frost Diagrams

- Frost diagram for nitrogen.
- The most stable form in acid is NH₃⁺.
- The most stable form in base is N₂.
- The steeper the line the greater the value of $E^\prime$.
- In fact, $E^\prime = – \text{ slope of the line}$. 

From Inorganic Chemistry by Shriver and Atkins, page 200.
Frost Diagram for Oxygen

- Point for $\text{H}_2\text{O}_2$ is at $(-1)0.77$ V = $-0.77$ V.
- Point for $\text{H}_2\text{O}$ is at $(-2)(+1.23)$ V = $-2.46$ V.
- The slope of the line from $\text{H}_2\text{O}$ to $\text{H}_2\text{O}_2$ is $+1.76$ V.

From Inorganic Chemistry by Shriver and Atkins, page 201.

Frost Diagram for Iron

- $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+} \rightarrow \text{Fe} \rightarrow -0.04$ V

Sketch the Frost diagram for iron.

More About Frost Diagrams

- A species that lies ABOVE the line connecting two adjacent species, it is unstable with respect to disproportionation.
- $2 \text{H}_2\text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{O}_2$
  - $\text{H}_2\text{O}_2 + 2e^- + 2\text{H}^+ \rightarrow 2 \text{H}_2\text{O} \quad E^\circ = +1.76$ V
  - $\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow 2 \text{H}_2\text{O} \quad E^\circ = +0.70$
  - $E^\circ_{\text{redox}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = +1.76$ V - $(+0.70$ V)$ = +1.06$ V


Frost Diagram for Manganese

- What is the most stable species?
- What is the best reducing agent?
- What is the best oxidizing agent?
- Comment on the stability of $\text{Mn}^{3+}$.