E^o and Thermodynamics

- E^o is related to ΔG^o, the free energy change for the reaction.
- ΔG° proportional to $-nE^\circ$

$$\Delta G^o = -nFE^o$$

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

E^o and ΔG^o

ΔG^o = - n F E^o

For a product-favored reaction

Reactants ----> Products

$\Delta G^o < 0$ and so $E^o > 0$

E^o is positive

For a reactant-favored reaction

Reactants <---- Products

$\Delta G^o > 0$ and so $E^o < 0$

E^o is negative

E° and Thermodynamics

- At any point on the way from pure reactants to equilibrium, reactants and products are not at standard conditions.
- $\Delta G = \Delta G^\circ + RT \ln Q$ (where Q is the reaction quotient)
- Because $\Delta G^\circ = -nFE^\circ$

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

Nernst Equation

Gives potential under nonstandard conditions

Nernst Equation

$$E = E^\circ - \frac{0.0257\ V}{n} \ln \frac{[\text{Products}]}{[\text{Reactants}]}$$

$$E = E^\circ - \frac{0.0592}{n} \log Q$$

- E = potential under nonstandard conditions
- n = no. of electrons exchanged
- If [P] and [R] = 1 mol/L, then E = E°
- If [R] > [P], then E is ______________ than E°
- If [R] < [P], then E is ______________ than E°

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 M and $[Ni^{2+}]$ = 0.010 M?
- Ni^{2+}(aq) ---> Ni(s) $E^\circ = -0.25$ V
- Cd^{2+}(aq) ---> Cd(s) $E^\circ = -0.40$ V
- Net equation: Cd(s) + Ni^{2+}(aq) ---> Cd^{2+}(aq) + Ni(s)
- $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = +0.15$ V
- E = +0.15 V – (0.0592/2) log (0.050/0.010)
- E = +0.15 V – 0.02 V = +0.13 V

Using the Nernst Equation

- What happens when your battery dies?
- The chemistry might have just reached equilibrium.
- At equilibrium E = 0
- So $E^\circ = (0.0592/n) \log K$
- E° used to find K and K used to find E°

Using the Nernst Equation: Calculate K

- **Calc. K_{sp} for $AgCl(s) \rightleftarrows Ag^+(aq) + Cl^-(aq)$**
- **Set up cell with AgCl/Ag electrode and Ag^+/Ag electrode**
- **Cathode: $AgCl(s) + e^- \text{--->} Ag(s) + Cl^-(aq)$**
- **Anode: $Ag(s) \text{--->} Ag^+(aq) + e^-(aq)$**
- **$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} =$**
  $(+0.222\ V) - (+0.799\ V) = -0.577\ V$
- **$\log K_{sp} = (1)(-0.577\ V)/0.0592\ V = -9.75$**
- **$K_{sp} = 1.8 \times 10^{-10}$**

Using the Nernst Equation: Concentration Cells

- **In a concentration cell there is no *net* oxidation or reduction, only a change in concentration.**
- **Now $E^\circ = 0$**
- **For example: $Fe(1, s) + Fe^{2+}(2, 0.010\ M) \rightleftarrows Fe^{2+}(1, 0.0050\ M) + Fe(2, s)$**
- **Cathode: $Fe^{2+}(aq) + 2e^- \text{--->} Fe(s)$ $E^\circ = -0.44\ V$**
- **Anode: $Fe(s) \text{--->} Fe^{2+}(aq) + 2e^-$ $E^\circ = +0.44\ V$**
- **$E^\circ_{cell} = 0.00\ V$**
- **$E = 0 - (0.0592\ V/2)\log(0.0050/0.010) = 0.0089\ V$**

Latimer diagrams

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

$$Fe^{3+} \xrightarrow{0.771\ V} Fe^{2+} \xrightarrow{-0.44\ V} Fe \quad (Fe^{3+} \to Fe: -0.04\ V)$$

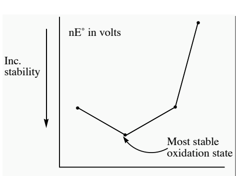
How do we derive the potential for $Fe^{3+} + 3e^- \text{-->} Fe(s)$?

Latimer diagrams

$$Fe^{3+} \xrightarrow{0.771\ V} Fe^{2+} \xrightarrow{-0.44\ V} Fe \quad (Fe^{3+} \to Fe: -0.04\ V)$$

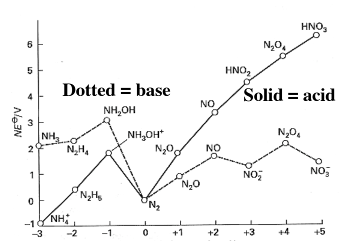
- **Convert E° values of ΔG° values and add to get ΔG°_{net}. Convert ΔG°_{net} to E°_{net}.**
- **$\Delta G^\circ_{net} = -(1)(F)(+0.771\ V) + \{-(2)(F)(-0.44\ V)\}$**
  $= +0.109\ (F)V$
- **$E^\circ net = -[+0.109\ (F)] / 3F$**
  $= -0.04\ V$

Frost Diagrams



- **Frost diagram is a plot of NE° versus oxidation number (N) for the couple**
  $X + Ne^- \text{--->} X^{n-}$ E°
- **Essentially a free energy plot because**
  $-\Delta G^\circ/F = NE^\circ$
- **The most stable oxidation state lies lowest in the diagram.**

Frost Diagrams



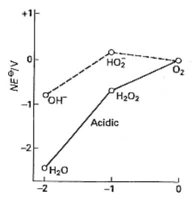
From *Inorganic Chemistry* by Shriver and Atkins, page 200.

- **Frost diagram for nitrogen.**
- **The most stable form in acid is NH_4^+.**
- **The most stable form in base is N_2.**
- **The steeper the line the greater the value of E°.**
- **In fact, E° = – slope of the line.**

Frost Diagram for Oxygen

+1.23 V

$O_2 \xrightarrow{+0.70\ V} H_2O_2 \xrightarrow{+1.76\ V} H_2O$



- **Point for H_2O_2 is at (–1)(0.77 V) = –0.77 V.**
- **Point for H_2O is at (–2)(+1.23 V) = –2.46 V**
- **The slope of the line from H_2O to H_2O_2 is +1.76 V.**

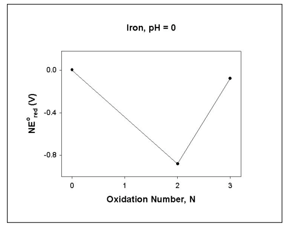
From *Inorganic Chemistry* by Shriver and Atkins, page 201.

Frost Diagram for Iron

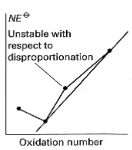
–0.04 V

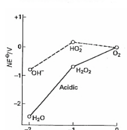
$Fe^{3+} \xrightarrow{0.771\ V} Fe^{2+} \xrightarrow{-0.44\ V} Fe$

Sketch the Frost diagram for iron.



More About Frost Diagrams



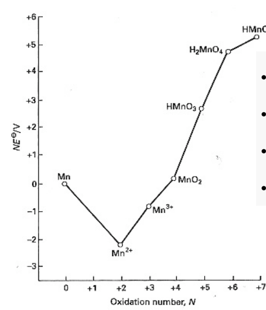


- **A species that lies ABOVE the the line connecting two adjacent species, it is unstable with respect to DISPROPORTIONATION.**
- **$2\,H_2O_2$ ---> $2\,H_2O + O_2$**
  - **H_2O_2 + 2e- + 2 H^+ ---> 2 H_2O E° = +1.76 V**
  - **O_2 + 2 H^+ + 2 e- ---> H_2O_2 E° = +0.70**

    $E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$ = +1.76 V – (+0.70 V)
  - **E°_{cell} = +1.06 V**

From *Inorganic Chemistry* by Shriver and Atkins, page 202.

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 Mn^{3+}.