Chem 116 Lecture 24 Notes (TC)
December 12, 2008

Voltage:
- Standard Cell Potential = $E°_{cell}$
- $E°_{cell}$ = In relation to
- *ΔG* is related to *ΔH, ΔS, and T*.

Calculating E_{cell} for non-standard conditions
- When it's at 25 C but not at a standard concentrations of 1.0M:
  > $E_{cell} = E°_{cell} – (0.0257/n) \ln Q$
  - or -
  > $E_{cell} = E°_{cell} – (0.0592/n) \log Q$

When it's also not a standard temperature of 25°C:
  > $E_{cell} = E°_{cell} – (RT/n\boldsymbol{F}) \ln Q$
  > ***F*** = Faraday's constant = 96,500 coulombs/mol

Electrolysis:
- Electrolysis reactions: reactions in which a non-spontaneous redox reaction is brought about by the passage of a current under a sufficient external electric potential.
- Electrolytic cells: This is where the same process of electrolysis occurs.
  > contains 2 electrodes (anode and cathode).
  > anode is where oxidation occurs (negative side of voltage source)
  > cathode is where reduction occurs (positive side of voltage source)
- Equations:
  > Coulombs = amperes * seconds
  > Electrical work:
    > $\Delta G = -nFE = w_{max}$ [the maximum useful electrical work obtained from a voltaic cell]
    > $w = nFE_{ext}$ [when external potential applied to cell]

Absolute Entropy:
- Symbol = (S)
- More disordered = higher absolute entropy
- More ordered = lower absolute entropy
- Absolute order = Perfect crystal lattice structure with no motion at zero absolute.
- No such thing as (absolute entropy = 0) except at the reference state of absolute order.
- The more complex the molecular structure:
  > higher the absolute entropy of the substance.
  > more options for configurations, rotations, and vibrations.
- (S) = (k)(ln W)   this is Boltzmann's equation and it's written on his gravestone
- W = degrees of freedom (a measure of how much freedom there is for particles in the system to rotate, vibrate, and move in other ways)
  > influenced by temperature, volume, and number of independently moving particles.

> if W increases, (S) increases.

- $\Delta S > 0$ = a change where the system becomes more disordered
- $\Delta S < 0$ = a change where the system becomes more ordered (less disordered)
- Hess's law applies to entropy because it is also a state function.

Gibbs Free Energy (ΔG)

- Measures absolute entropy change of the entire universe (actually, it's the opposite sign of this - according to the second law of thermodynamics, during any process the entropy of the entire universe increases, and during any spontaneous process the Gibbs free energy decreases)

ΔG for the system is negative for any change of the system that is spontaneous

- Equation:

> $\Delta G = \Delta H - T\,\Delta S$
>
> ΔG = *Gibbs Free Energy*
>
> ΔH = *Enthalpy change*
>
> ΔS = *Entropy change*
>
> T = Absolute temperature (in Kelvin)

- So ΔG depends on enthalpy change and entropy change

ΔG and K_{eq}

- When the system is at another temperature other than standard temperature of 25°C

> $\Delta G = \Delta G° + (RT)(\ln Q)$

- At equilibrium $\Delta G = 0$ and $Q = K_{eq}$

> $\Delta G° = -(RT)(\ln K_{eq})$