Stuff

- Call Mom
- Quiz 7 and HW 4 results posted-please check
- New Weeks' pop quizzes
  - Tues-quiz on use of the EC series-qualitative and quantitative
  - Thurs
    - reactions from "words"
    - ΔG^o, K and E^o

You should be comfortable with..

- Oxidation numbers
- Breaking down redox processes
- Balancing redox equations
- Verbal/written description of redox processes
- use of the EC series to predict whether a redox process is favored and to calculate E^o
- The nature of galvanic cells
  – anode and cathode and the processes that occur there
  – shorthand notation

Summary-the key equations

- As always, the equations and needed constants will be provided. There are three very critical issues in properly applying the relationships
  - T **must be in K**, when needed
  - the value for the potential must be correct and the sign noted properly. Keys: ($E^o>0=>\Delta\Delta\Delta G^o<0$ & K>1)
  - n-the number of electrons transferred in the balanced equation must be properly determined

- $\triangle G^o=-RTlnK$
  - T in deg K
  - R=.008314KJ/K

- $\triangle G=-nFE$
  - n is the number of electrons transferred in the balanced redox eqn
  - F=96.5KJ/V

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

- $K=e^{-\triangle Go/RT}$
  - T in deg K
  - R=.008314KJ/K

- at 25^oC $lnK=nE^o/0.0257$ or $logK=16.9nE^o$
  - n as above

Examples

- What are E^o, ΔG^o and K for the oxidation of NO to NO_3^- by AgCl(s)
- What are E^o, ΔG^o and K for the reduction of Ni^{2+} by Al(s)

Recall-you're never actually at standard conditions

- Real electrochemical systems are seldom under standard conditions. Even a system initially under such conditions will immediately move away from that state as soon as the reaction begins.
- Regardless of the intent of the designer, the reaction will run in the spontaneous direction (beginning at Q=1).
  - A system proposed which has a negative E^o will run right to left. Since all these systems must run to equilibrium (Q=K and E=0), it follows that the |potential| of the reaction must constantly decrease as it proceeds.
  - As Q goes toward K, E goes toward 0. Always keep in mind that it's the Q=1 starting point against which all these changes are gauged.
- The following give an overview vs the Q=1 condition
  - K>1 and E^o>0 The reaction will proceed L to R until equilibrium is reached. During that time, Q will constantly increase as the potential moves toward zero.
  - K<1 and E^o<0 The reaction will proceed R to L until equilibrium is reached. During that time, Q constantly decreases as the potential moves toward zero.

- Calculation of the potential of the system at non-standard conditions is done using the Nernst Equation(at 25°C)

$$E = E^o - \frac{0.0257}{n} \ln Q$$

- Use of the Nernst equation is relatively straightforward. It requires a balanced redox equation, E^o and n. A quick examination of the equation should make it apparent that electrochemical potentials don't change much,even with relatively large changes in Q. This is consistent with the very large (or very small values) of K produced from seemingly small values of E^o.

One Example

- $9H_2O(l) + 3Sb_2O_5(s) + 4Al(s) => 6SbO^+(aq) + 4Al^{3+}(aq) + 18OH^-(aq)$
  $E^o= -2.46V$
  $[SbO^+]:0.40M$
  $[Al^{3+}]:1.0M$
  $[OH^-]:0.10M$

- n=12-you can get that by simple looking at one of the ½ reactions
  - $4Al=>Al^{3+} + 12$ e-

- $E=-2.46-0.0257/12*ln([0.40]^6[1.0]^4[0.10]^{18}/1)$
  Q is evaluated
  $E=-2.46-0.0257/12*ln(4.10*10^{-21})$
  The terms are solved and combined.
  $E=-2.46-0.00214*-46.9$
  Finally, E is calculated
 $E=-2.36$

- is this the expected result?

Suppose the nonspontaneous reaction is desirable

- It is often necessary to drive an electrochemical process in the nonspontaneous direction.
  - This is due to the fact that the natural electrochemical equilibria attained on the earth place materials in an "undesirable" form. Examples of this are the metals, most of which are found as oxides of some type, the halogens, all of which are found as halides, or hydrogen, found in water.
  - Converting these back into the elements can be done by chemical redox processes (smelting of metals) or electrolysis(for the production of sodium, aluminum, chlorine, hydrogen and others).
- To drive the reaction in the nonspontaneous direction an external potential, normally significantly higher than the E^o must be applied. The extra voltage, much of it due to the nature of the electrodes, is called the overpotential.
- When an external potential drives the reaction in the nonspontaneous direction, the cell is called electrolytic. What are the signs of the anode and cathode in such a cell?

- Materials will be produced at both electrodes.
- The main issue in analyzing such a cell, since the potential is largely an engineering issue, is the determination of the amount of material produced at each electrode.
- This is determined by calculating the number of electrons that flows thru the cell in the time period of interest and combining it with the electron requirements of the desired process.
- One does not need a balanced redox equation to analyze such processes, but the electrode reactions must be properly identified.
- Needed relationships
    - Current(amp)*t(secs)=coulombs
    - coulombs/96,500=moles of e-
    - (moles of e-)/(e-s per mole of product)=moles of product
    - moles product*gfw=mass of product
- Example: aluminum is produced by the electrolysis of a compound of Al $^{3+}$. If a current of 100amps flows through the cell for one hour, how many grams of aluminum would be produced?
    - 100amps*(3600s) = 360000coulombs
    - 360000/96500=3.73Faradays
    - 3.73/3=1.24moles of Al=> 33.5grams (kind of pitiful)
    - Worldwide production of aluminum is roughly 50million tons/year. Imagine the electricity consumption.
    - The increase in electricity cost combined with Al recycling have resulted in the closing of all of the aluminum production mills in the NW.

- If the process below is driven electrolytically, how many grams of material will be produced at the cathode by a current of 73.8 amps flowing for 5.19hours?
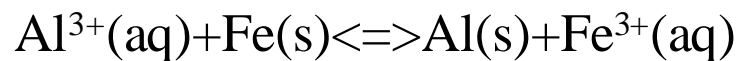
  $Al^{3+}(aq)+Fe(s)<=>Al(s)+Fe^{3+}(aq)$

- If the process below is driven electrolytically, how many grams of material will be produced at the anode by a current of 76.4 amps flowing for 0.481hours?

  $MnO_4^-(aq)+Ag + Cl^-(aq)<=>Mn^{2+}(aq)+AgCl(s)$