Noteworthy

- These notes should cover this week and week 13
- Exam 3-Acid/bases, solubility and Second Law
- Lots of nomenclature mixed in
- Lab this week is straightforward-report sheet will be completed and turned in at the end of the period.
- Next week is the Qual Unknown-you have to have a flow diagram for Groups I and III combined in order to do the expt.
- The posted scores are current and complete-please check for accuracy
- Anyone considering withdrawing needs to do so by Thurs at the latest. You should see me if you're unsure.

Basic ideas in electrochemistry

- Sections 4.6 to 4.10 (p.145-168) should be reviewed. This includes acid-base which should be reviewed for the coming exam.
- Oxidation-process whereby one or more electrons is lost. The species undergoing oxidation is also called the reducing agent (RA)
- Reduction-process whereby one or more electrons is gained. Species being reduced is also called the oxidizing agent(OA).
- Just as acid-base chemistry is treated as proton transfer, oxidation-reduction chemistry is viewed as electron transfer. As these processes are generally reversible (and equilibria), they can be described as:

$$\text{OA} + \text{RA} \Leftrightarrow \text{RA} + \text{OA}$$

- Tracking of electrons is most easily done by use of oxidation numbers (see p. 155-158).
  - The oxidation number is simply the comparison of the electron count for an element in a compound or ion with that of the element in its elemental form, where it is assigned an oxidation number of 0.
  - One needs to be mindful that oxidation numbers are a bookkeeping formalism and are not a true measure of electron distribution in a compound.
  - an **increase** in oxidation number is indicative of an **oxidation**
  - a **decrease** in oxidation number is indicative of a **reduction**

Oxidation Numbers

- You should be aware that oxidation numbers are used to track electron changes, and will not represent the actual distribution of electrons in a complex species
- General Rules
  - Elements in their elemental forms have ON=0
  - A monoatomic ion has an oxidation number equal to its charge
  - In chemical compounds or polyatomic ions(there is a hierarchy here, a higher rule trumps a lower one.
    - fluorine is always 1-
    - oxygen is 2- except in peroxides(1-). These compounds have O-O single bonds
    - other halogens are 1- except for interhalogen compounds or when bound to oxygen. In an interhalogen compound, the more electronegative element is assigned ON=1-
    - H is 1+ except when bound to a metal (NaH)
    - the sum of the oxidation numbers must equal the charge on the compound or ion.
- What are the oxidation number of all of the atoms in the following:$Na_2C_2O_4$, $Pd(OH)_4$, $NaBF_4$, Au_2S_3, $H_2PO_4^-$, Na_3PO_3, $Cu(NO_3)_2$, ClF_3, $POCl_3$

Breaking down Redox Processes

- Describe each of the following in as many different ways as possible-I'll explain what that means.
- $ClO_4^- + Th \Leftrightarrow Cl^- + Th^{4+}$
- $Cl_2 + Be \Leftrightarrow Cl^- + Be_2O_3^{2-}$
- $AsO_2^- + Fe^{2+} \Leftrightarrow As + Fe^{3+}$
- $Sb_2O_3 + Mo \Leftrightarrow Sb + Mo^{3+}$
- $ClO_2 + F^- \Leftrightarrow ClO_2^- + F_2$
- $Al^{3+} + SO_2 \Leftrightarrow Al + SO_4^{2-}$

Balancing redox equations

- The balancing of redox equations is a special challenge as the balancing must result in neither a production or consumption of electrons. Further, there is often no "mass linkage" between the oxidizing and reducing agents ($Na(s) + MnO_4^- \Leftrightarrow Na^+ + Mn^{2+}$) and for a given redox process there are often numerous mass balanced equations.
  - There are a number of different methods for balancing redox equations. We will be using the ion-electron method. A slight modification in the approach will be suggested. It's interesting that this method makes no use of oxidation numbers. The half reaction method is also presented in your text.
  - If we don't actually use them to balance redox equations, what good are oxidation numbers?
- Acidic vs basic solution. Many redox reactions "require" that the medium be either basic or acidic.
  - In real terms this describes the availability of H^+ or OH^- as products or reagents. Chemically their roles normally involve extra "O" and are summarized by the following equations,which can be written in either direction:
  - acidic $2H^+(aq) + "O" \Leftrightarrow H_2O$
  - basic $2OH^-(aq) \Leftrightarrow H_2O + "O"$

Two Examples

- $Cr_2O_7^{2-}(aq) + Fe(s) \Leftrightarrow Cr^{3+}(aq) + Fe^{2+}(aq)$ (acid)
- Separate the reaction into two half reactions:
  - $Cr_2O_7^{2-}(aq) \Leftrightarrow Cr^{3+}(aq)$
  - $Fe(s) \Leftrightarrow Fe^{2+}(aq)$
- Mass balance each half reaction without concern for oxygen or hydrogen
  - $Cr_2O_7^{2-}(aq) \Leftrightarrow 2Cr^{3+}(aq)$
  - $Fe(s) \Leftrightarrow Fe^{2+}(aq)$
- Complete mass balance for H and O, based upon nature of the medium
  - $14H^+(aq) + Cr_2O_7^{2-}(aq) \Leftrightarrow 2Cr^{3+}(aq) + 7H_2O$
  - $Fe(s) \Leftrightarrow Fe^{2+}(aq)$
- Charge balance each half reaction by adding the appropriate number of electrons
  - $6e^- + 14H^+(aq) + Cr_2O_7^{2-}(aq) \Leftrightarrow 2Cr^{3+}(aq) + 7H_2O$
  - $Fe(s) \Leftrightarrow Fe^{2+}(aq) + 2e^-$
- Combine the half reactions in a manner that achieves e - balance
  - $6e^- + 14H^+(aq) + Cr_2O_7^{2-}(aq) \Leftrightarrow 2Cr^{3+}(aq) + 7H_2O$ (x1)
  - $Fe(s) \Leftrightarrow Fe^{2+}(aq) + 2e^-$ (x3)
- Combine the half reactions and "clean up" as necessary
  - $14H^+(aq) + Cr_2O_7^{2-}(aq) + 3Fe(s) \Leftrightarrow 2Cr^{3+}(aq) + 3Fe^{2+}(aq) + 7H_2O$

- $Cr^{3+}(aq) + MnO_2(s) \Leftrightarrow Mn^{2+}(aq) + CrO_4^{2-}(aq)$ (basic)
- half reactions:
  - $Cr^{3+}(aq) \Leftrightarrow CrO_4^{2-}(aq)$
  - $MnO_2(s) \Leftrightarrow Mn^{2+}(aq)$
- both half reactions are already mass balanced except for O, so go directly to that step(basic solution)
  - $8OH^-(aq) + Cr^{3+}(aq) \Leftrightarrow CrO_4^{2-}(aq) + 4H_2O$
  - $2H_2O + MnO_2(s) \Leftrightarrow Mn^{2+}(aq) + 4OH^-(aq)$
- add electrons
  - $8OH^-(aq) + Cr^{3+}(aq) \Leftrightarrow CrO_4^{2-}(aq) + 4H_2O + 3e-$
  - $2e- + 2H_2O + MnO_2(s) \Leftrightarrow Mn^{2+}(aq) + 4OH^-(aq)$
- common factor is 6
  - $8OH^-(aq) + Cr^{3+}(aq) \Leftrightarrow CrO_4^{2-}(aq) + 4H_2O + 3e-$ (x2)
  - $2e- + 2H_2O + MnO_2(s) \Leftrightarrow Mn^{2+}(aq) + 4OH^-(aq)$ (x3)
  - $16OH^-(aq) + 2Cr^{3+}(aq) + 6H_2O + 3MnO_2(s) \Leftrightarrow 2CrO_4^{2-}(aq) + 8H_2O$ $3Mn^{2+}(aq) + 12OH^-(aq)$
  - this reaction is “cleaned up” by removing 12 OH- and 6 H_2O from each side, yielding the following final result
  - $4OH^-(aq) + 2Cr^{3+}(aq) + 3MnO_2(s) \Leftrightarrow 2CrO_4^{2-}(aq) + 2H_2O + 3Mn^{2+}(aq)$

- $ClO_4^- + NO_2 \Rightarrow Cl^- + NO_3$ (acid)
- same as above in base
- $MnO_2 + Sb \Rightarrow Mn^{2+} + Sb_2O_3$ (base)
- same as above in acid
- $Cl_2 \Leftrightarrow Cl^- + ClO_3^-$

So You Thought Oxidation Numbers were simple

C_2H_6O

CH_3CHO

CH_3CO_2H

CH_3NH_2

CH_3NO_2

Assignment of oxidation states to the above requires (in general) a correct Lewis structure.

ON=Valences e^-s -(LP e^-s + assigned electrons)

assigned electrons-All bonding electrons are assigned to the element with the greater electronegativity. Electrons in homonuclear bonds are split

What’s what

- Where in the periodic table would you expect to find the oxidizing agents? Where are the reducing agents?
- In the absence of some “extra” process, what will necessarily happen on a planet over the billions of years? Why has gold been so valuable through the ages?
- What are examples of “extra” processes and what is the ultimate extra process?

Electrochemical Potential

- The measure of the tendency for the electron transfer is the electrochemical potential(E), measured in volts.
- The determination of E is relatively straightforward. One sets up a voltaic cell(see Fig 17.2-p 792)
  - the two half reactions are isolated (separate beakers)
  - a salt bridge and external circuit are added. The salt bridge permits movement of ions between the two half cells and the external circuit carries the current. The electrode which is the **site of oxidation is the anode**, the **site of reduction is the cathode**.
  - The potential is measured using a voltmeter. If the measured potential is +, the reaction is spontaneous. A voltaic cell which is spontaneous is termed galvanic. The potential of a redox process is a state function.
- A very critical point is that the measured potential for the overall reaction is the sum of the potentials for the two half reactions-who’s responsible for that?
- One other note-reversing the reaction reverses the sign of the potential.
- A few notes on electrical terms-note these are clearly interrelated
  - volt-unit of electrical pressure-1.00volt is the potential required to produce a current of 1.00amps against a resistance of 1.00ohms
  - Coulomb-unit of charge-dimensionless unit of charge=$6.24*10^{18}$-the amount of charge when a current of 1 ampere flows for 1 second
  - ampere-current 1coulomb/second
  - Faraday-1 mole of electrons 96,500coulombs=1 Faraday

Standard Half Potentials

- Since any redox process can be viewed as follows
  - $OA_1 \Rightarrow RA_1 \quad E_1$
  - $RA_2 \Rightarrow OA_2 \quad E_2$
  - $OA_1 + RA_2 \Rightarrow RA_1 + OA_2 \quad E_{rxn} = E_1 + E_2$
- This underscores two issues:
- the usefulness in knowing the potential for a half reaction
- the impossibility of measuring the potential of a half reaction
- I think this is called a conundrum-what to do?
- cheat-SHE
- standard conditions require that all []s=1.00M and all pressures=1.00atm

F_2(g) +2e- => 2F-	+2.87V
Ce $^{4+}$(aq)+ e- => Ce $^{3+}$(aq)	+1.61V
MnO_4^-(aq) + 8H$^+$ + 5e- => Mn $^{2+}$(aq) + 4H_2O(l)	+1.51V
Cl_2(g) +2e- => 2Cl$^-$(aq)	+1.36V
O_2(g) + 4H$^+$ => 2H_2O(l)	+1.23V
NO_3^-(aq)+ 4H$^+$ (aq) +3e- => NO(g)+ 2H_2O(l)	+0.96V
Ag+ (aq) + e- => Ag(s)	+0.80V
Fe $^{3+}$(aq) + e- => Fe $^{2+}$(aq)	+0.77V
Cu $^{2+}$ (aq) +2e- => Cu(s)	+0.34V
2H$^+$(aq) + 2e- => H_2(g)	0.00V
Pb $^{2+}$ (aq) +2e- => Pb(s)	-0.13V
Fe $^{2+}$(aq) +2e- => Fe(s)	-0.44V
Zn^2+ (aq) + 2e- => Zn(s)	-0.76V
2H_2O(l) + 2e- => H_2(g) + 2OH$^-$ (aq)	-0.83V
Fe $^{3+}$(aq) +3e- => Fe(s)	-0.44V
Al^{3+} (aq) + 3e- => Al(s)	-1.66V
Li$^+$(aq) + e- => Li(s)	-3.05V

Using the Std Reduction Potentials

- The electrochemical series arranges half reactions as reductions in order of decreasing potential. Thus, the species shown on the reactant side of the reactions are all oxidizing agents. Those on the product are the reducing agents
- Any “reactant” will oxidize all “products” below it. Be certain to look at the product side for the actual species being oxidized.
- Likewise, any “product” will reduce every “reactant” above it.
- You determine the overall potential be taking the difference between the two potentials-this process may seem very awkward at first.
    - $E_{cell}=E_{red} + E_{ox}$
    - since, for the process which is occurring as an oxidation: $E_{ox}=-E_{red}$
    - $E_{cell}=E_{red} - E_{red(ox)}$
    - key check -if the oxidizing agent is above the reducing agent the potential will be positive.

- Use of the EC Series has both a qualitative and quantitative aspect. In many cases, the qualitative aspect is sufficient, for, as will be seen, nearly any positive potential ensures complete reaction. On exams and quizzes you will be asked for both qualitative and quantitative responses to use of the EC series. Each of the following assumes standard conditions.
- Will Ag$^+$ oxidize Pb(s)
    - what is E ^{o} for this reaction
- Will Zn reduce Al^{3+}
    - what is E ^{o} for this reaction
- Will Cl_2 be reduced by Fe $^{2+}$
    - what is E ^{o} for this reaction
- Will NO be oxidized by Pb $^{2+}$
    - what is E ^{o} for this reaction

Echem to date

- Have covered:
- Oxidation numbers
- Balancing redox equations
- The vocabulary of electrochemistry
- The galvanic cell
- Electrochemical potential and use of the electrochemical series
- In addition-principles of electrolysis and Faraday’s laws were discussed.

Basic Redox Vocabulary

- Write reactions for each of the following:
- oxidation of metallic nickel by BiO^+
- reduction of Zn^{2+} by hydroxide ion
- reaction of Fe^{2+} with Hg^{2+}
- reaction of Cd^{2+} with NO_2
- AgI acting as an oxidizing agent toward Sn^{2+}
- What’s wrong with
- The oxidation of Cr by Cl^-
- The reduction of Co^{2+} by Ag^+

Cell Notation

- As was noted earlier, galvanic cells normally consist of two distinct regions, one housing the oxidation half and the other the reduction half. There is a simplified notation form that allows one to represent the cell easily(text p 798-799).
- The oxidation is written on the left and the reduction on the right. starting with the anode material and ending with the cathode material.
- phase boundaries represented with single vertical lines “ |”
- the physical separation between the two half cells is a double vertical line “||” if it’s a salt bridge and with a single broken vertical line, “ ⁝ ”, if it’s a liquid junction
- within each have cell, the species are written in a reactant-product order, separated by commas if they are in the same phase. Acid/base components should be included
- The electrode material may be actively participating in the redox chemistry (active electrode) or merely providing surface for the electron transfer (passive or inert electrode, usually graphite or Pt)
- Represent the following as galvanic cells(assume the reactions are spontaneous as written)
- $Tl(s) + Cd^{2+} \Leftrightarrow Tl^+ + Cd(s)$
- $Pb(s) + MnO_4^- \Leftrightarrow Pb^{2+} + Mn^{2+}$ (acid)
- $O_2(g) + Sn^{2+} \Leftrightarrow H_2O + Sn^{4+}$

Practical Galvanic Cells -batteries

- Batteries represent the most common application of the electrochemical cell. The first batteries were relatively simple devices but represented an enormous step forward in the initial efforts towards the practical use of electricity.
- Primary cells-designed to provide current one time
- Secondary-rechargeable
- Fuel cells-reactants continuously fed to the electrodes

Potential, Free Energy and Equilibrium

- Logic requires that if the potential is an unambiguous measure of spontaneity, it must be "relatable" the other indicators of spontaneity, ΔG and K.
- Before proceeding, it should be noted that E should be viewed as representing the "per electron" potential. In order to scale it up to a "per reaction" value, it needs to be multiplied by the number of moles of electrons in the balanced reaction, normally represented as "n". In general, you do not have to balance the reaction to get n, as the half reactions are in the EC Series.
- $\Delta G = -nFE$ (F=96.5KJ/V.mol). If one uses the standard potential E^o, then the result is the standard free energy.

$$\ln K = \frac{nFE^0}{RT}$$

- at 25^oC $\ln K = nE^o/0.0257$
- A key observation, hopefully obvious from the above equations, is that relatively small potentials lead to very large (or very small) values for ΔG and K.
- In utilizing the above, one does not need to balance the redox equation, but care must be taken in determining the values for E^o and n.

Summary-the key equations

- $\Delta G^o = -RT\ln K$
  - T in deg K
  - R=.008314KJ/K
- $\Delta G = -nFE$
  - n is the number of electrons transferred in the balanced redox eqn
  - F=96.5KJ/V
- $\Delta G^o = -nFE^o$
- $K = e^{-\Delta Go/RT}$
  - T in deg K
  - R=.008314KJ/K
- at 25^oC $\ln K = nE^o/0.0257$ or $\log K = 16.9nE^o$
  - n as above

- A reaction has an equilibrium constant of $2.28*10^{-15}$ at 478K. What is the standard free energy change in KJ/mole?
- $\Delta G=-RT\ln K$ $\ln(2.28*10^{-15})=-33.7$
  $\Delta G=-0.008314*478*-33.7=134KJ$
- A reaction has a standard free energy change of -191KJ/mole at 380K. What is the equilibrium constant ?
- $K=e^{-\Delta G/RT}$
  $K=e^{--191/(.008314*380)}=1.8*10^{26}$

- $Ag^+ + S_2O_3^{2-} \Rightarrow Ag + SO_3^{2-}$ $E^o=1.38V$
- $Ag^+ +1e^- \Rightarrow Ag$
  $S_2O_3^{2-} \Rightarrow SO_3^{2-}+4e^-$
- n=4
- $\ln K=(n*E^o)/.0257=(4*1.38)/.0257=215$
- $K=e^{215}=2.36*10^{93}$
- $\triangle G^o=-nFE^o=-4*96.5*1.38=-532KJ$

- $I_3^- + Fe^{2+} \Rightarrow I^- + Fe^{3+}$ $E^o=-0.226V$
- $I_3^- +2e^- \Rightarrow I^-$
  $Fe^{2+} \Rightarrow Fe^{3+}+1e$
- n=2
- $\ln K=(n*E^o)/.0257=(2*-0.226)/.0257=-17.6$
  $K=e^{-17.6}=2.27*10^{-8}$
- $\Delta G^o=-nFE^o=-2*96.5*-0.226=43.6KJ$

Cell notation

- $V^{2+}(aq)+ClO_2^-<=>V^{3+}(aq)+Cl^-(aq)$ (acid)
- $C(s)|V^{2+}(aq),V^{3+}(aq)||ClO_2^-,H^+,Cl^-(aq)|C(s)$
- $Rb(s)+Ce^{4+}(aq)<=>Rb^+(aq)+Ce^{3+}(aq)$
- $Rb(s)|Rb^+(aq)||Ce^{4+}(aq)|Ce^{3+}(aq)$
- $Au^+(aq)+HAsO_2(aq)<=>Au^{3+}(aq)+As(s)$ (acid)
- $C(s)|Au^+(aq),Au^{3+}(aq)||HAsO_2(aq),H^+|As(s)|C(s)$
- The other way
- $C(s)|Cu^+(aq),Cu^{2+}(aq)||Mg^{2+}(aq)|Mg(s)$
- $Cu^+(aq)+Mg^{2+}(aq)<=>Cu^{2+}(aq)+Mg(s)$
- $C(s)|ClO_2(g)|ClO_3^-(aq)||MnO_4^-(aq),H^+,MnO_4^{2-}(aq)|C(s)$
- $ClO_2(g)+MnO_4^-(aq)<=>ClO_3^-(aq)+MnO_4^{2-}(aq)$ (acid)

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
- The relationships between E,K and ΔG.

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: $(E^o>0=>\Delta\triangle\Delta G^o<0$ & $K>1)$
  - n-the number of electrons transferred in the balanced equation must be properly determined
- $\Delta G^o=-RTlnK$
  - T in deg K
  - R=.008314KJ/K
- $\Delta G=-nFE$
  - n is the number of electrons transferred in the balanced redox eqn
  - F=96.5KJ/V
- $\Delta G^o=-nFE^o$
- $K=e^{-\Delta Go/RT}$
  - T in deg K
  - R=.008314KJ/K
- at 25°C $lnK=nE^o/0.0257$ or $logK=16.9nE^o$
  - n as above

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

- $9H_2O(l) + 3Sb_2O_5(s) + 4Al(s) \Rightarrow 6SbO^+(aq) + 4Al^{3+}(aq) + 18OH^-(aq)$
  E^o= -2.46**V**
  $[SbO^+]$:0.40**M**
  $[Al^{3+}]$:1.0**M**
  $[OH^-]$:0.10**M**
- n=12-you can get that by simple looking at one of the ½ reactions
  - $4Al \Rightarrow Al^{3+} + 12\ e^-$

- $E=-2.46-0.0257/12*\ln([0.40]^6[1.0]^4[0.10]^{18}/1)$
  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?

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

Batteries

- What are the major issues regarding battery design?
- Lead Storage:
  - $Pb(s) + PbO_2(s) + 2H^+ + 2HSO_4^- \Rightarrow 2PbSO_4(s) + 2H_2O(l)$
  - What makes these so dangerous?
  - Is a service free battery really what it says?
  - What's the proper way to jump start a car (which no one ever does)
- Dry Cell-not really dry -uses a paste
  - $Zn(s) + 2MnO_2(s) + 2NH_4^+(aq) \Rightarrow Zn^{2+}(aq) + Mn_2O_3(s) + 2NH_3(aq) + H_2O(l)$
- Alkaline
  - $Zn(s) + 2MnO_2(s) \Rightarrow ZnO(s) + Mn_2O_3(s)$
- Mercury
  - $Zn(s) + HgO(s) \Rightarrow ZnO(s) + Hg(l)$
- Ni/Cad
  - $Cd(s) + 2NiO(OH) + 2H_2O(l) \Rightarrow Cd(OH)_2 + 2Ni(OH)_2$
- Lithium
  - $Li(s) + MnO_2(s) \Rightarrow LiMnO_2(s)$
- Do you see anything interesting about many of the Q's above? What are the advantages and disadvantages of this?

Corrosion

- Since the earth has an oxidizing atmosphere, any material below the reduction of O_2 in the electrochemical series (which includes most metals) is subject to natural oxidation. With metals these processes are usually undesirable and are called corrosion.
- Rust
  - anode: $Fe(s) \Rightarrow Fe^{2+} + 2e^-$ (pits develop at the anode)
  - cathode: $O_2(g) + 4H^+(aq) + 4e^- \Rightarrow 2H_2O(l)$
  - further oxidation of the Fe^{2+} occurs in solution
  - solid Fe_2O_3 ppts in the cathode region
- The prevention of unwanted oxidation is of considerable interest and takes many forms.
- Natural oxide coatings which are often applied by electrolytic anodization. This will only work if the oxide adheres strongly to the metal surface(aluminum). Unfortunately, iron doesn't have this characteristic. However, stainless steel, an alloy of iron, does.
- Paint-big in the military
- Grease
- Metal plating (chrome on steel, for example). Fine as long as the coating maintains its integrity

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- Use of a sacrificial anode-with iron this is often zinc and the process is called galvanization, if a coating is applied. In the days when iron pipe was common in household plumbing, it was sometimes protected by burying a block of zinc the in yard and running a wire from the zinc to the iron pipes. This made the pipe cathodic.
  - Galvanization is done by either electrolysis or "hot dipping"
- Using an external charge to keep the metal slightly cathode, electrically. this is sometimes used to protect ships in salt water.

Combining Potentials

- Consider the series below
  - Fe $^{3+}$ e- => Fe $^{2+}$ E^o = +0.77V
  - Fe $^{2+}$ + 2e- => Fe(s) E^o= -0.44V
  - Fe $^{3+}$ + 3e- => Fe (s) E^o= -0.04V
- Why isn't the potential for the third reaction simply the sum of the first two?
- Since there must be a relationship between the potentials, what mathematical combination of the first two potentials will yield the third?

- Fe $^{3+}$ e- => Fe $^{2+}$ E^o = +0.77V
- Fe $^{2+}$ + 2e- => Fe(s) E^o= -0.44V
- Fe $^{3+}$ + 3e- => Fe (s) E^o= -0.04V
- unlike redox processes, potential for a "series" are not additive, since they are " normed" to one electron. However, free energies are additive.
- $\Delta G_1 + \Delta G_2 = \Delta G_3$
- $-n_1FE^o_1 + -n_2FE^o_2 = -n_3FE^o_3$
- This can readily be arranged to the following:

$$\frac{n_1E_1^0 + n_2E_2^0}{n_3} = E_3^0$$

$$\frac{+0.77 + 2*(-0.44)}{3} = -0.04$$

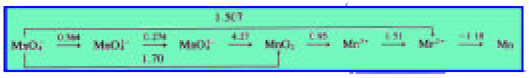
Wait a minute-that's not different

- In actuality all of the combining of potentials is based upon free energies. If we're combining two half reactions to get Ecell, the equation below is used. What's the key to it's being simplified?

$$\frac{n_1E^0_{red} + n_2E^0_{red\,(ox)}}{n_3} = E^0_{cell}$$

Latimer Diagram

- The Latimer Diagram for Mn



LeChatelier and Electrochemistry

- Nernst Equation

  $E = E^o - (RT/nF)\ln Q$
- System is at equilibrium so E=0. Is a voltage produced by each of the following and, if so, what is its sign?
  - reagent added or removed
  - product added or removed
  - volume increased
  - T increased or decreased

A few more Comments on LeChatelier

- Consider the following generic redox rxn
- $2A(aq) + 3B(aq) + 6H^+(aq) \Leftrightarrow C(aq) + 2D(aq) + 3H_2O$
- When the reaction is not at equilibrium:
  - what is the sign of E when the reaction is occurring L to R
  - R to L
- If the system is at equilibrium(E=0), what is the sign of the potential resulting from each of the following:
- addition of C
- decrease in V
- increase in the pH

What’s a Fuel Cell

- A fuel cell is “simply” a galvanic cell wherein the oxidizing and reducing agents are continuously fed (fueled) to the electrodes.
- hydrogen cell-descriptive(not balanced)
  - H_2 => $2H^+$ anode
  - O_2 => $2OH^-$ cathode
  - $H_2 + O_2$ => H_2O
- Political comments
- Does a hydrogen fuel cell or a hydrogen based economy represent a viable alternative to the internal combustion engine?
- How expensive do we want oil to become? Whatever that number is-it’s on the way there. Every prediction made in the 1970s (during the oil embargo) about the future of energy has been proven to be incorrect. That’s both scientific and political predictions.

Concentration Cells

- A concentration cell derives its potential from the difference in concentration between the right and left sides. The pH meter is such an application.
- $M|M^+(aq, L)||M^+(aq, R)|M$
- The cell reaction is $M^+(aq, R)$ => $M^+(aq, L)$
- Nernst equation: $E = E^o - (RT/nF) \ln Q$
- But $E^o = 0$! (Do you see why?)
- $\ln Q = [L]/[R]$
- So for a conc. cell, $E = -(RT/nF) \ln ([L]/[R])$
- Recall that the potential doesn’t change much for relatively large changes in Q. Thus, **extremely small concentrations** can be detected.
- If one of the electrodes is designed such that the concentration is 1.00M, the resultant potential can easily be converted into a concentration
  - $E = -(0.0257/n) \ln[L]$ if([R]=1.00)
- A cell is designed such that [R]=1.00M. If n=2 and the measured potential is 0.10V what is [L]?
  - $-0.10(2/.0257)=\ln[L]$ $[L]=4.2*10^{-5}$