

# Today's Information

- Probably not on campus tomorrow
- Performance on Redox Balancing was superb. Exam will also have two equations-slightly more difficult.
- Exam will cover:
  - All of Electrochemistry
  - All of Second Law

# Batteries

- Text-section 18.9(p 786) has detailed discussions of common batteries
- What are the major issues regarding battery design?
- Lead Storage:
  - $\text{Pb(s)} + \text{PbO}_2\text{(s)} + 2\text{H}^+ + 2\text{HSO}_4^- \Rightarrow 2\text{PbSO}_4\text{(s)} + 2\text{H}_2\text{O(l)}$
  - 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
  - $\text{Zn(s)} + 2\text{MnO}_2\text{(s)} + 2\text{NH}_4^+\text{(aq)} \Rightarrow \text{Zn}^{2+}\text{(aq)} + \text{Mn}_2\text{O}_3\text{(s)} + 2\text{NH}_3\text{(aq)} + \text{H}_2\text{O(l)}$
- Alkaline
  - $\text{Zn(s)} + 2\text{MnO}_2\text{(s)} \Rightarrow \text{ZnO(s)} + \text{Mn}_2\text{O}_3\text{(s)}$
- Mercury
  - $\text{Zn(s)} + \text{HgO(s)} \Rightarrow \text{ZnO(s)} + \text{Hg(l)}$
- Ni/Cad
  - $\text{Cd(s)} + 2\text{NiO(OH)} + 2\text{H}_2\text{O(l)} \Rightarrow \text{Cd(OH)}_2 + 2\text{Ni(OH)}_2$
- Lithium
  - $\text{Li(s)} + \text{MnO}_2\text{(s)} \Rightarrow \text{LiMnO}_2\text{(s)}$
- 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-see fig 18.13 for a graphic of the process
  - 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  $Fe_2O_3$  ppt 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

- 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
  - $\text{Fe}^{3+} + \text{e}^- \Rightarrow \text{Fe}^{2+}$   $E^\circ = +0.77\text{V}$
  - $\text{Fe}^{2+} + 2\text{e}^- \Rightarrow \text{Fe}(\text{s})$   $E^\circ = -0.44\text{V}$
  - $\text{Fe}^{3+} + 3\text{e}^- \Rightarrow \text{Fe}(\text{s})$   $E^\circ = -0.04\text{V}$
- 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?

- $\text{Fe}^{3+} + \text{e}^- \Rightarrow \text{Fe}^{2+} \quad E^\circ = +0.77\text{V}$
- $\text{Fe}^{2+} + 2\text{e}^- \Rightarrow \text{Fe(s)} \quad E^\circ = -0.44\text{V}$
- $\text{Fe}^{3+} + 3\text{e}^- \Rightarrow \text{Fe(s)} \quad E^\circ = -0.04\text{V}$
- unlike redox processes, potential for a “series” are not additive, since they are “normed” to one electron. However, free energies are additive.
- $\Delta G_1 + \Delta G_2 = \Delta G_3$
- $-n_1FE^\circ_1 + -n_2FE^\circ_2 = -n_3FE^\circ_3$
- This can readily be arranged to the following:

$$\frac{n_1 E_1^0 + n_2 E_2^0}{n_3} = E_3^0$$

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

# 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  $E_{cell}$ , the equation below is used. What's the key to it's being simplified?

$$\frac{n_1 E_{red}^0 + n_2 E_{red(ox)}^0}{n_3} = E_{cell}^0$$

## LeChatelier and Electrochemistry

- Nernst Equation

$$E = E^{\circ} - (RT/nF)\ln Q$$

- 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



# 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)
  - $\text{H}_2 \Rightarrow 2\text{H}^+$  anode
  - $\text{O}_2 \Rightarrow 2\text{OH}^-$  cathode
  - $\text{H}_2 + \text{O}_2 \Rightarrow \text{H}_2\text{O}$
- Political comments
- Does a hydrogen fuel cell represent a viable alternative to the internal combustion engine?
- How expensive do we want oil to become?

# Concentration Cells

- A concentration cell derives its potential from the difference in concentration between the right and left sides. Your text, sec 18.7 describes the pH meter-a similar application.
- $M|M^+(aq, L)||M^+(aq, R)|M$
- The cell reaction is  $M^+(aq, R) \Rightarrow M^+(aq, L)$
- Nernst equation:  $E = E^\circ - (RT/nF) \ln Q$
- But  $E^\circ = 0$  ! (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  $[L]$ ?
  - $-0.10(2/.0257)=\ln[L]$        $[L]=4.2*10^{-5}$