Electrochem II

The New Stuff

Sage Advice

- Use your **POTENTIAL**
- **WORK** as hard as you can
- be **FREE** and **ENERGY** filled.

Electromotive Force

- EMF = volts
- Volts = work/charge
- V= J/C where J is joules and C is Coulombs of charge.
- $-w = q\epsilon$ so work = charge x volts
- $\text{work}_{max} = q\epsilon_{max}$

Got Entropy?

- In order to get current to flow, some is always WASTED. It increases the ENTROPY of the universe.
- One unfortunate consequence.
  - Can't get full voltage out of a cell that is actually doing anything useful.

Example

- At battery at rest is measured instantaneously to have 2.50 V.
- When it is working it measures 2.10 V.
- How much work is produced by the battery if 1.33 moles of e- pass through at 2.10V?

Example

- q = nF
- charge = number of moles x 96,485 C/mole e- [96,485 Coulombs is called a Faraday]
- w= -qЄ

-1.33 moles	96,485C	2.10 J
	1 mole e	1 C

- = -3.21×10^{5} J

What is the efficiency?

- Calculate theoretical max work and divide actual work by theoretical or take short cut.

- All of the stuff except voltage in the factor label problem is constant so
- V_{actual}/V_{max} = efficiency
- 2.10 V/2.50 V = 84% !!!! Easy!!!

Free Energy (just ask…)

Free Energy (not sold in stores…)

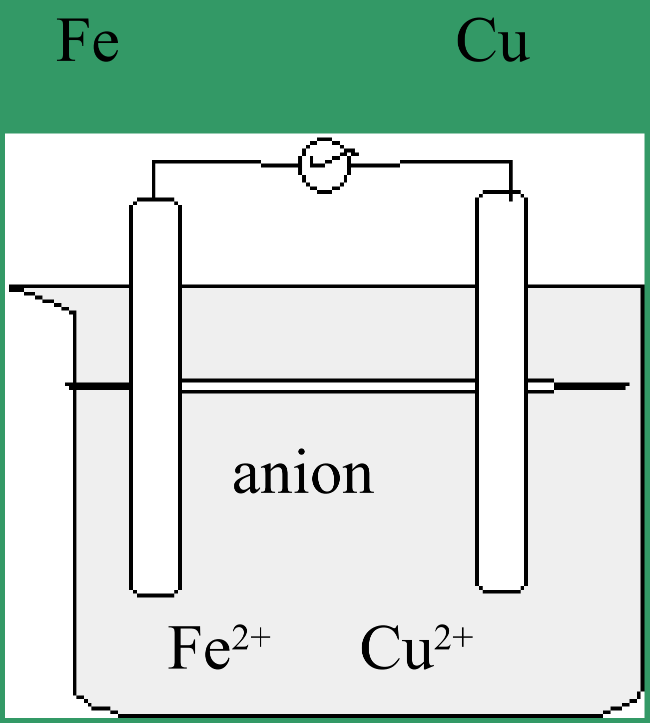
- If current flows the reaction is spontaneous. The max energy or work you can get out is ΔG, the Gibbs Free Energy. So…

Calculating ΔG of a cell

- $\Delta G = -nF\mathcal{E}$
- n = number of moles of e-
- F = 96,485 Coulombs of charge
- $\mathcal{E}$ = cell voltage.
- For a reaction to go, $\Delta G < 0$

Example

- Calculate $\Delta G°$ for the reaction: $Cu^{2+}(aq) + Fe(s) \Longrightarrow Cu(s) + Fe^{2+}$
- $Cu^{2+} + 2e^- \Longrightarrow Cu$ above
- $Fe \Longrightarrow Fe^{2+} + 2e^-$ below
- $\Delta G = -nF\mathcal{E}$
- $\Delta G = 2 \times 96{,}485 \times 0.78$
- -1.5×10^5 J



0.34 V + 0.44V = 0.78V

Non-standard concentration

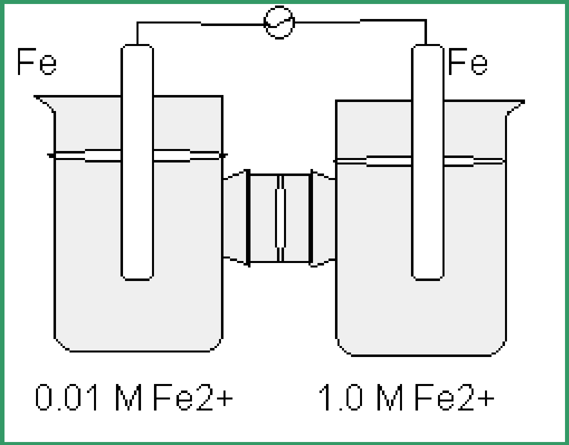
- Recall LeChatelier's principle.
- Turn to a partner. If you are on the left, predict whether the voltage of a cell would be higher, lower, or the same if the concentration of dissolved ions at the anode are above standard.
- If you are on the right, predict if the voltage would be higher, lower or same if dissolved chemicals at cathode are above standard.

Thumbs up, down, or level

- It may help to recognize that at the anode, oxidation forces the anode to dissolve.
- Plating out occurs at the cathode due to reduction

Concentration Cell (Mr K's classroom :)

- Again with LeChatelier's principle, predict the flow of electrons in this cell.
- Point left or right.
- Turn to your neighbor and discuss your reasoning.



Non-standard concentration

- If the concentration of the dissolved ions at the anode are higher than standard, cell produces less voltage
- If the concentration of the dissolved species at the cathode is above standard, the voltage will be a tad higher.

Nernst Equation (see board)

- Use for correcting a cell with non-standard concentrations.
- $\epsilon = \epsilon^{\circ} - \frac{RT}{nF} \ln(Q)$
- At 25C this is
- $\epsilon = \epsilon^{\circ} - \frac{0.0591}{n} \log(Q)$

Example

- If $\mathcal{E}°$ cell for $2Al(s) + 3Mn^{2+} \Longrightarrow 2Al^{3+} + 3\,Mn(s)$ is 0.48 V
- What is the voltage of a cell that has $[Mn^{2+}] = 0.50$ M and $[Al^{3+}] = 1.50$ M (both non standard)
- Balance half reactions
- Count number of moles of e-
- Use Nernst equation:
  $$\mathcal{E}_{cell} = \mathcal{E}° - \frac{0.0591}{n} \log(Q)$$
-

Q? (The reaction quotient)

- $2\ Al \Longrightarrow 2\ Al^{3+} + 6e^-$
- $3\ Mn^{2+} + 6e^- \Longrightarrow 3\ Mn$
- n= 6 moles e-
- $Q = \dfrac{[Al^{3+}]^2}{[Mn^{2+}]^3}$
- $\dfrac{(1.50)^2}{(0.50)^3} = 18$

Example contd.

- $\varepsilon_{cell} = 0.48 - \frac{0.0591}{6} \log(18)$
- Actual voltage is 0.47 V

Electro-stoichiometry