Lecture 27 – Chapter 19, Sections 5-6
Faraday, Nernst, and Fuel Cells

- Faraday’s Constant – charge of an electron
- Nernst Equation – nonstandard cell potential
- Applications – Fuel Cells

Cell Potential and Free Energy

- We know E > 0 for spontaneous reactions
- Also ΔG < 0 for spontaneous reactions
- This is no coincidence…

$$\Delta G = -nFE$$

- Of course, this is still true at 1 bar, 298.15 K, 1 M, etc.

$$\Delta G^\circ = -nFE^\circ$$

- n is the number of moles of electrons
- F is the faraday constant (often a lovely script $\mathscr{F}$)

$$F = 96485.34 \text{ C/mol} = e\,N_\text{A}$$

Relating G to E

- Remember our Zn and Cu galvanic cell

$$Zn \rightarrow Zn^{2+} + 2e^- \qquad 0.7618\text{ V} \quad \text{(oxidation)}$$

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad 0.3419\text{ V} \quad \text{(reduction)}$$

$$E^\circ_{cell} = 0.3419 + 0.7618 = 1.1037\text{ V}$$

Overall rxn is: $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

(2 electrons are transferred per mole reactants)

- So, then the ΔG° must be

$$\begin{aligned} -nFE^\circ &= -2(96485\text{ C/mol})(1.1037\text{ V}) \\ &= -2(96485\text{ C/mol})(1.1037\text{ J/C}) \\ &= -212{,}980\text{ J/mol} \\ &= -212.98\text{ kJ/mol} \end{aligned}$$

Relating E to K_{eq}

- Of course, we should also be able to relate E to Keq

$$-nFE^\circ = \Delta G^\circ = -RT\ln K_{eq}$$

$$E^\circ = \frac{RT}{nF}\ln K_{eq}$$

$$E^\circ = \frac{0.05916\ \mathrm{V}}{n}\log K_{eq}$$

- So, for our Cu and Zn reaction

$$E^\circ = \frac{0.05916\ \mathrm{V}}{2}\log K_{eq}$$

$$\log K_{eq} = \frac{2\times 1.1037\ \mathrm{V}}{0.05916\ \mathrm{V}}$$

$$K_{eq} = 10^{37.312} = 2.05\times 10^{37}$$

What if it's cold out?

- Since we know how to calculate ΔG at non-standard conditions, we can also calculate E

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$\text{but} \quad \Delta G^\circ = -nFE^\circ$$

$$-nFE = -nFE^\circ + RT \ln Q$$

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

$$E = E^\circ - \frac{0.05916\ \mathrm{V}}{n} \log Q \qquad (\text{at } 298\ \mathrm{K})$$

So, if we have 1.2 M Zn^{2+} and 0.8 M Cu^{2+} what is our cell potential? (Assuming we are at 298 K)

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)} \qquad E^\circ = 1.1037\text{ V}$$

$$E = E^\circ - \frac{0.05916\text{ V}}{n}\log Q \qquad (\text{at } 298\text{ K})$$

25%	1.	1.0516 V
25%	2.	1.0985 V
25%	3.	1.1089 V
25%	4.	1.1558 V

1	2	3	4	5

What causes a larger effect?

A 10 % change in concentrations

or

A 10 % change in temperature?

$$E = E^\circ - \frac{RT}{nF}\ln Q$$

25%	1.	Concentrations
25%	2.	Temperature
25%	3.	They are about the same
25%	4.	Neither one has any significant effect

1	2	3	4	5

Volts and Current

- Volts give the potential energy on each electron V ~ J/C
- Current is the number of electrons per time A ~ C/s

$$\text{Moles of electrons} = n = \frac{I\,t}{F}$$

Redox Applications

- I said there were many back when we started Chapt 19
- Today focus on the most common: Batteries
- And also potentially one of the most useful: Fuel Cells

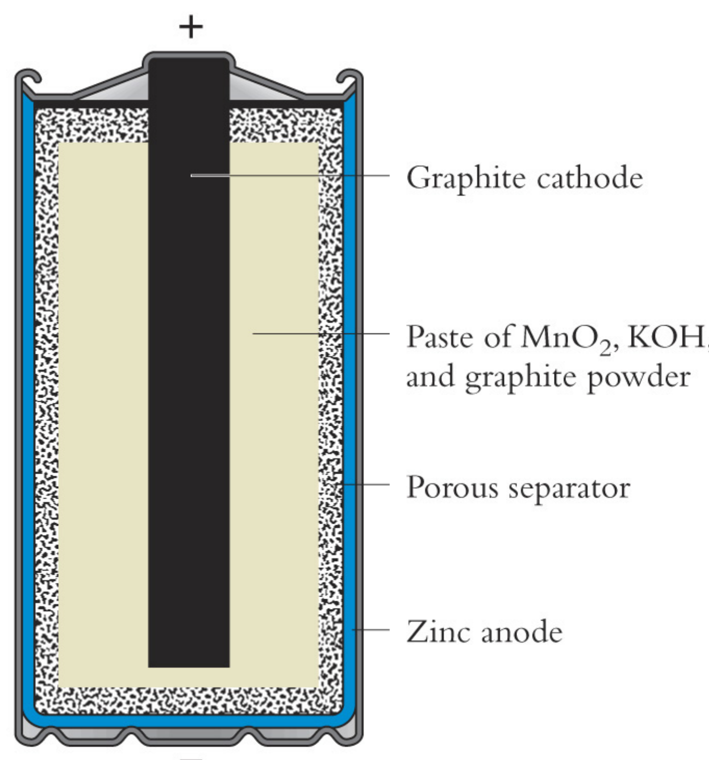
Alkaline Dry Cell:

$$2MnO_{2\,(s)} + H_2O_{\,(l)} + 2e^- \rightarrow Mn_2O_{3\,(s)} + 2OH^-_{\,(aq)}$$

$$Zn_{\,(s)} + 2OH^-_{\,(aq)} \rightarrow Zn(OH)_{2\,(s)} + 2e^-$$

$$2MnO_{2\,(s)} + H_2O_{\,(l)} + Zn_{\,(s)} \rightarrow Mn_2O_{3\,(s)} + Zn(OH)_{2\,(s)}$$

E is about 1.5 V
'Dry' because the paste contains little water compared to 'wet' cell (car battery).



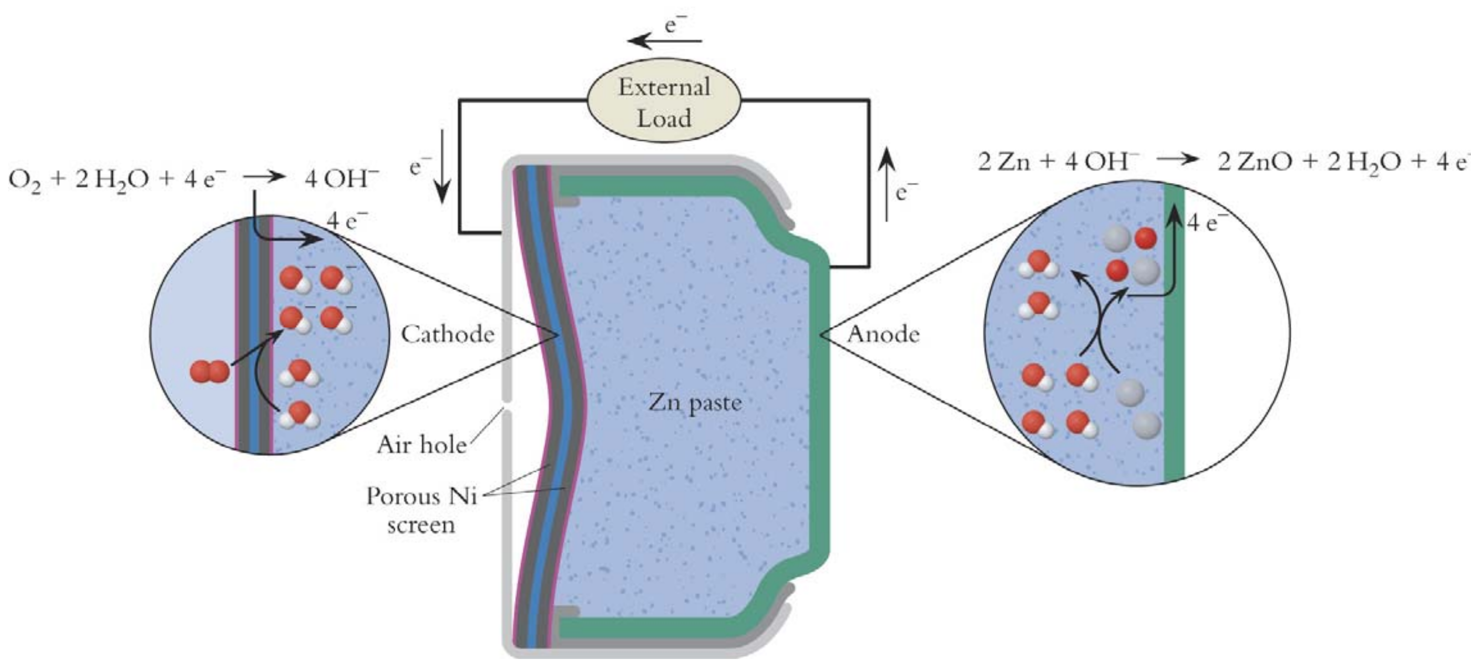
Zinc-air (watch) Battery

- Uses atmospheric oxygen as reactant
- All materials always in constant concentration (activity) so the cell's voltage is always the same
  - Aside from temperature variation of course

$$O_{2\,(g)} + 2\,H_2O_{(l)} + 4\,e^- \rightarrow 4\,OH^-_{(aq)}$$

$$2\,Zn_{(s)} + 4\,OH^-_{(aq)} \rightarrow 2\,ZnO_{(s)} + 2\,H_2O_{(l)} + 4\,e^-$$

$$O_{2\,(g)} + 2\,Zn_{(s)} \rightarrow 2\,ZnO_{(s)}$$



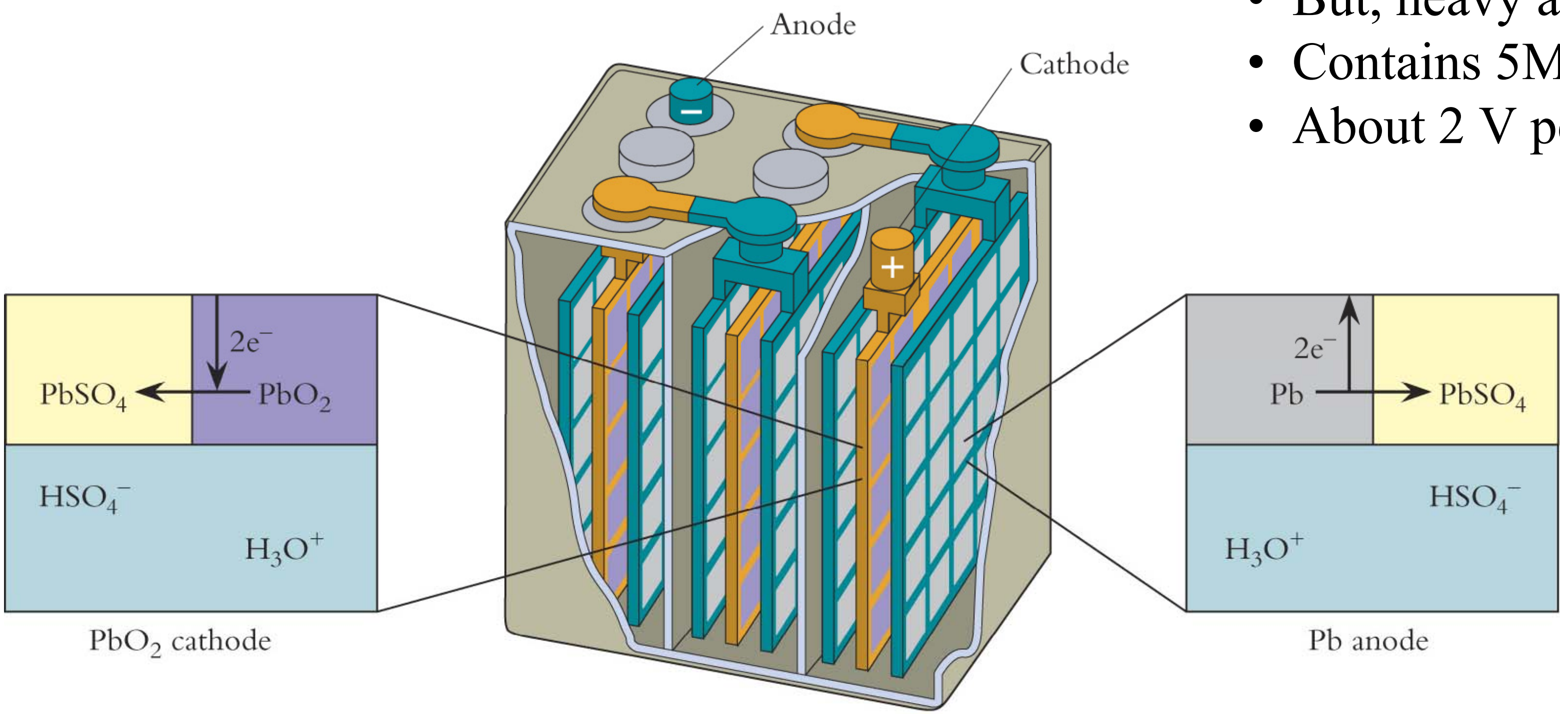
Lead Storage Battery (wet cell)

$$PbO_{2\,(s)} + HSO_4^-{}_{(aq)} + 3H_3O^+{}_{(aq)} + 2e^- \rightarrow PbSO_{4\,(s)} + 5H_2O_{(l)}$$

$$Pb_{(s)} + HSO_4^-{}_{(aq)} + H_2O_{(l)} \rightarrow PbSO_{4\,(s)} + H_3O^+{}_{(aq)} + 2e^-$$

$$Pb_{(s)} + 2HSO_4^-{}_{(aq)} + PbO_{2\,(s)} + 2H_3O^+{}_{(aq)} \rightarrow 2PbSO_{4\,(s)} + 4H_2O_{(l)}$$

- Provides large current
- Rechargeable many times
- But, heavy and big
- Contains 5M H_2SO_4
- About 2 V per cell



Fuel Cell

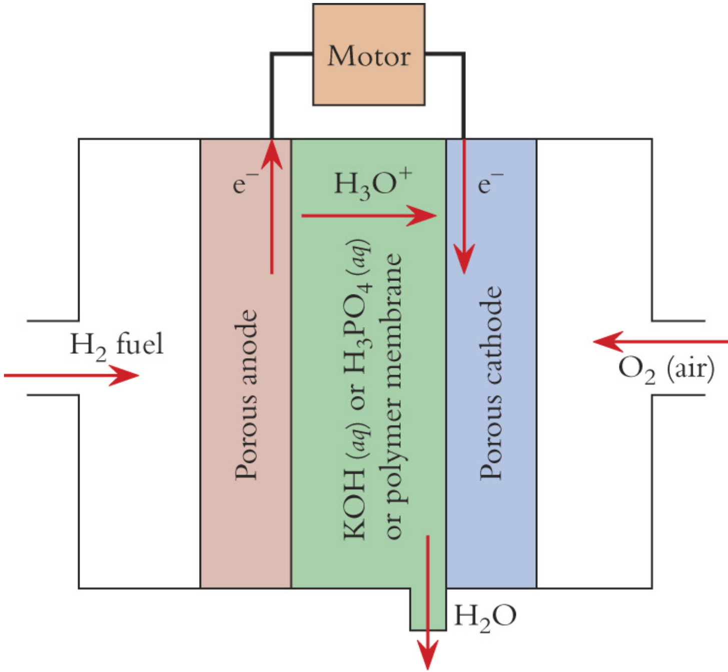
- Essentially the combustion of hydrogen
- But reduction of O_2 and oxidation of H_2 carried out in separate places.
- Makes lots of electricity and only waste is H_2O!
- But, H_2 is hard to make and dicey to transport

Fuel Cell:

$$2\ H_{2\,(g)} + 4\ H_2O_{\,(l)} \rightarrow 4\ H_3O^+_{\,(aq)} + 4\ e^-$$

$$O_{2\,(g)} + 2\ H_2O_{\,(l)} + 4\ e^- \rightarrow 4\ OH^-_{\,(aq)}$$

$$2\ H_{2\,(g)} + O_{2\,(g)} \rightarrow 2\ H_2O_{\,(l)}$$



Fuel Cell

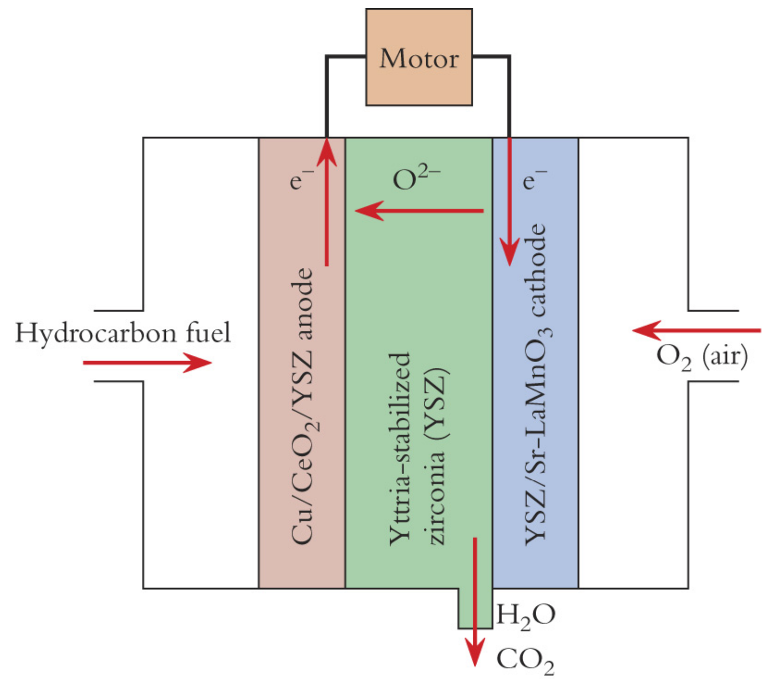
- Fuel cell vehicles with H_2 may be tough
- One alternative is to 'burn' hydrocarbons
- Still get CO_2 (greenhouse gas) as product
- But, do not get any nasty CO, NO, NO_2, etc.
- Also get more energy per unit fuel than combustion engine

Hydrocarbon Fuel Cell:

$$2\,C_4H_{10} + 26\,O^{2-} \rightarrow 8\,CO_2 + 10\,H_2O + 52\,e^-$$

$$13\,(O_2 + 4\,e^- \rightarrow 2\,O^{2-})$$

$$2\,C_4H_{10} + 13\,O_2 \rightarrow 8\,CO_2 + 10\,H_2O$$



Today

- Work on CAPA #16 – but not due until Wed!
- **Good chance to review old material**!

Wednesday

- Finish CAPA #16
- Keep reviewing

Thursday

- Chemistry Seminar 4:00