April 17, 2002

- ➢ **<u>Exam #3 - TODAY!</u>**
  - ✓7 pm Kalkin 001
- ➢ Demo Today!
- ➢ No Quiz Friday
- ➢ Demo Friday?

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More Uses for Nernst

- ➢ Equilibrium Constant Determinations

$\boxed{\text{Pb (s)}|\text{Pb}^{2+} \text{ (sat'd PbCl}_2\text{ (aq))}||\text{Pb}^{2+} \text{ (0.100 } M\text{)}|\text{Pb (s)}}$

Another concentration cell

Ox $\quad Pb(s) \rightarrow Pb^{2+}(aq) + 2e^-$

Red $\quad Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$

$Pb^{2+}(0.100\ M) \rightarrow Pb^{2+}(\text{sat'd})$

Measure E_{cell}: ***0.0237 volts***

$\boxed{\text{What is } K_{sp} \text{ for } PbCl_2\text{?}}$

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The Nernst Solution

- Nernst will provide $[Pb^{2+}]$:

$$\mathbf{E_{cell} = E^{o}_{cell} - (0.0592/n)LogQ}$$

$$\mathbf{Q} = \frac{[Pb^{2+}]_{anode}}{[Pb^{2+}]_{cathode}} = \frac{[Pb^{2+}]_{sat'd}}{0.100\ M}$$

$$\mathbf{0.0237 = 0.000 - (0.0592/2)Log([Pb^{2+}]/0.100)}$$

$$\mathbf{[Pb^{2+}] = 1.6 \times 10^{-2}}\ \boldsymbol{M}$$

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Finally, Equilibrium

- Solubility Equilbrium:

$$PbCl_2\ (s) \leftrightarrows Pb^{2+}\ (aq) + 2Cl^-\ (aq)$$

S 2S

Substitute into K_{sp} expression:

$$K_{sp} = [Pb^{2+}][Cl^-]^2 = S(2S)^2 = 4S^3$$

$$K_{sp} = 4(\mathbf{1.6 \times 10^{-2}})^3 = \underline{\boldsymbol{1.6 \times 10^{-5}}}$$

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Batteries

- What happens if we *allow current to flow* in a Galvanic Cell?
  - ✓Oxidation and Reduction reactions occur
  - ✓Concentrations change
  - ✓$Q \rightarrow K$ (equilibrium)
  - ✓$E_{cell} \rightarrow 0$ (*dead battery!*)
- Is the reaction ***reversible***?
  - ✓Battery can be recharged
  - ✓Apply a potential sufficient to drive the *reverse reaction*

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Example: Pb-Acid Battery

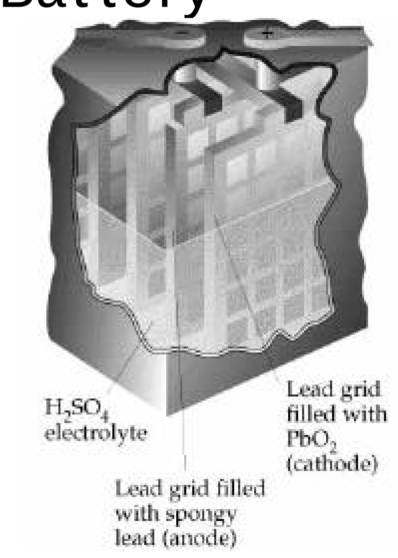
Anode: Pb-Sb alloy grid filled with spongy Pb

Cathode: PbO_2 coating

$$Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \rightarrow$$
$$2PbSO_4 + 2H_2O$$
$$E_{cell} \approx 2.0 \text{ volts}$$

As it discharges:

- $PbSO_4$ coats electrodes
- Electrolyte gets diluted



Charge it up!

- Apply a potential > E_{cell} (opposite polarity)

  Forces the *reverse reaction*:

$$PbSO_4 \rightarrow Pb + PbO_2 + H^+ + SO_4^{2-}$$

When battery discharges *completely:*

- $PbSO_4$ completely covers electrodes
- Can't recharge!
- ***Dead Battery***

When battery is *overcharged:*

- No $PbSO_4$ left to react
- Electrolysis of water
- H_2 and O_2 form
  - ✓Ruins Pb and PbO_2 coatings
  - ✓***Explosive!***

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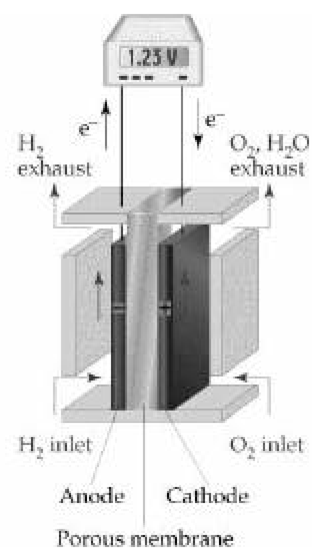
Fuel Cells

- Just an "Open" system battery
- Products and reactants are continuously replenished



Electrolysis

- Force a *nonspontaneous reaction* to occur by applying a potential:
  - ✓Greater than E_{cell}
  - ✓Opposite polarity
- Why Do It?
  - ✓Useful chemistry can happen
  - ✓Can *quantify* the extent of the reaction

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Quantifying Electrolysis: Faraday's Laws

1. The amount of chemical change is proportional to the quantity of electrical charge that passes through an electrolytic cell

   Measure current: 1 Ampere = 1 Coulomb/sec

   Get charge: # Coulombs = current (Amps) x time (sec)

2. A given quantity of electricity produces the *same number of equivalents of any substance* in an electrolysis process:

   1 equivalent = 1 mol e^- in a half-reaction

   ✓ *Relate charge (Coulombs) to equivalents using Faraday's Constant* (96,487 C/mol e^-)

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Illustrative Example

- What mass of Cu is deposited if a current of **1.50 A** flows for **1.00 hour** in the electrolysis of a $CuSO_4$ solution?

The reaction: Cu^{2+} (aq) + $2e^-$ $\rightarrow$ Cu (s)

time $\rightarrow$ charge $\rightarrow$ mol e^- $\rightarrow$ mol Cu $\rightarrow$ g Cu

$$1.00 \text{ hr} \times \frac{60 \text{ min}}{1 \text{ hr}} \times \frac{60 \text{ sec}}{1 \text{ min}} \times \frac{1.5 \text{ C}}{\text{sec}} \times \frac{1 \text{ mol } e^-}{96{,}487 \text{ C}} \times \frac{1 \text{ mol Cu}}{2 \text{ mol } e^-} \times \frac{63.55 \text{ g Cu}}{1 \text{ mol Cu}} =$$

= ***1.78 g Cu***

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