

Chapter 17

Electrochemistry



Redox Reactions

- Electrochemistry is the study of batteries and interconversion of chemical and electrical energy.
- Based on redox (oxidation-reduction) reactions in which one element gains electrons and another loses electrons.
 - These two processes MUST happen together.
- Have to assign oxidation numbers to determine (see Chapter 4).

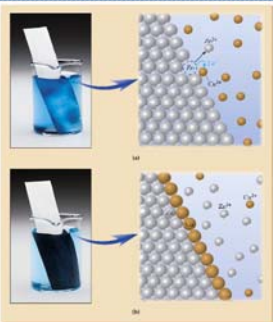
Oxidation Numbers

- Elements in their natural states are 0.
- Elements in binary ionic compounds are the same as their charges.
- H: usually +1, except with alkali metals (LiH, NaH, etc.)
- O: usually -2, except in peroxides (H_2O_2 , K_2O_2)
- The non-oxygen element in a polyatomic ion has to be determined from the other oxidation numbers.

Redox Reactions

- Oxidation: loss of electrons
- Reduction: gain of electrons
 - LEO the lion goes GER or OIL RIG
- The substance oxidized is also called the reducing agent (it caused the other substance to be reduced). And vice versa.
- $\text{Cu(s)} + \text{AgNO}_3 \rightarrow \text{Ag(s)} + \text{Cu(NO}_3)_2$

$\text{Cu(s)} + \text{AgNO}_3(\text{aq})$



Redox Reactions

- $\text{CH}_4(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$
- $\text{Na(s)} + \text{HCl(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2(\text{g})$
- For each reaction:
 - What is oxidized, reduced?
 - What is the oxidizing agent? Reducing agent?
- Combustion, decomposition, combustion, and single-replacement reactions are all redox.

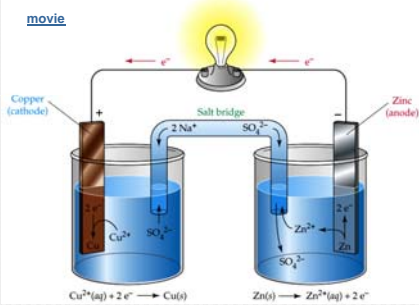
Balancing Redox Reactions

- $\text{Cr}^{3+}(\text{aq}) + \text{Be}(\text{s}) \rightarrow \text{Cr}(\text{s}) + \text{Be}^{2+}(\text{aq})$
- To balance (notice the charges), we break it up into two **half reactions**, the oxidation half and reduction half.
- We have to balance electrons.
- Oxidation: $(\text{Be}(\text{s}) \rightarrow \text{Be}^{2+}(\text{aq}) + 2\text{e}^-) \times 3$
- Reduction: $(\text{Cr}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Cr}(\text{s})) \times 2$
- $2\text{Cr}^{3+}(\text{aq}) + 3\text{Be}(\text{s}) \rightarrow 2\text{Cr}(\text{s}) + 3\text{Be}^{2+}(\text{aq})$

Galvanic Cells

Electron motion in a cell

movie



Galvanic Cells

- Oxidation reaction: occurs at the anode (mass decreases over time)
- Reduction reaction: occurs at the cathode (mass increases over time)
- Electrons are transferred across a wire (through a voltmeter)
 - Voltage is the cell potential, E (or Electromotive Force, EMF)
- Salt bridge - soluble salt solution used to neutralize the ions that build up in each solution.

Batteries

- Galvanic cells are describing the batteries we use in everyday life.
- Batteries die when 1) the anode is completely consumed, 2) the cathode solution is consumed, or 3) the salt bridge runs out of ions.
- Bigger batteries only last longer, they don't have more volts. Volts are determined by the chemicals used.

Short-hand Notation

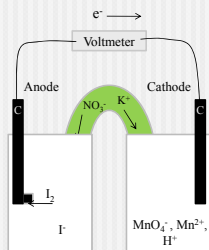
- $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$
- $\text{Zn(s)} | \text{Zn}^{2+}(\text{aq}) || \text{Cu}^{2+}(\text{aq}) | \text{Cu(s)}$
- Anode | anode ion || cathode ion | cathode
- This is always written in order of the oxidation half reaction, then the reduction half reaction.
- Not all half reactions use a solid metal electrode.

Inert Electrodes

- If the electrode needed is a soluble ionic compound or a gas, we can use Graphite or Platinum as the electrode.
- These substances allow electrons to transfer but don't take place in the reaction.
- Figure 17.4

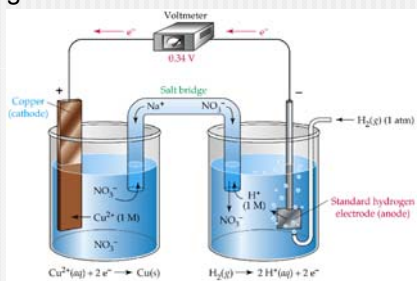
Galvanic Cells

- Oxidation: $2 \text{I}^-(\text{aq}) \rightarrow \text{I}_2(\text{s}) + 2\text{e}^-$
- Reduction: $\text{MnO}_4^-(\text{aq}) + \text{H}^+(\text{aq}) + 5\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$
- Total equation: $2 \text{MnO}_4^-(\text{aq}) + 16 \text{H}^+(\text{aq}) + 10 \text{I}^- \rightarrow 2 \text{Mn}^{2+}(\text{aq}) + 4 \text{H}_2\text{O}(\text{l}) + 5 \text{I}_2(\text{s})$



Galvanic Cells - Pt electrode

■ Figure 17.4



Standard Cell Potential, E°

- Gases at 1 atm
- Solutions at 1 M
- Temperature at 298 K (25°C)
- Standard potential for any galvanic cell is the sum of the half-cell potentials.
 - $E^\circ_{\text{cell}} = E^\circ_{\text{ox}} + E^\circ_{\text{red}}$
- $\text{H}_2(\text{g}) | \text{H}^+(\text{aq}) || \text{Cu}^{2+}(\text{aq}) | \text{Cu}(\text{s})$
- Write the half reactions.

Reduction Potentials

- We can use the table of Reduction Potentials of half reactions to determine the cell potential of a galvanic cell.
- Table 17.1: All potentials are listed at **reduction** potentials.
- How do we determine **oxidation** potentials?

TABLE 19.1 Standard Reduction Potentials at 25°C

Reduction Half-Reaction	E° (V)
$F_2(g) + 2e^- \rightarrow 2F^-(aq)$	2.87
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$	1.78
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.51
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.33
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	1.23
$Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$	1.09
$Ag^+(aq) + e^- \rightarrow Ag(s)$	0.80
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	0.77
$O_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2O_2(aq)$	0.70
$I_2(s) + 2e^- \rightarrow 2I^-(aq)$	0.54
$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$	0.40
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	0.34
$Sr^{2+}(aq) + 2e^- \rightarrow Sr(s)$	0.15
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$	-0.13
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	-0.26
$Co^{3+}(aq) + 2e^- \rightarrow Co^{2+}(aq)$	-0.40
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	-0.45
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	-0.76
$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	-0.83
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	-1.66
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	-2.37
$Na^+(aq) + e^- \rightarrow Na(s)$	-2.71
$Li^+(aq) + e^- \rightarrow Li(s)$	-3.04

Stronger oxidizing agent (red arrow pointing up) and Weaker oxidizing agent (orange arrow pointing down) are indicated on the left. Weaker reducing agent (blue arrow pointing down) and Stronger reducing agent (blue arrow pointing up) are indicated on the right.

Cell Potentials

- Once you find the potentials for the half reactions, you add the values together to get the overall cell potential.
- E° is in Volts (V = J/C or C = J/V or J = CV)
- All cell potentials are compared to hydrogen (SHE: **standard hydrogen electrode**)
- $H_2(g) \rightarrow 2H^+ + 2e^-$ E°_{red} = 0 V
- Standard reduction potentials (E°_{red}) are compared to SHE.

Cell Potentials

- Positive E°_{cell} means the reaction is product-favored.
 - The reaction will go forward until the battery dies.
 - A negative E°_{cell} means the reaction won't really happen.
- Therefore, we want two half reactions that yield the most positive E°_{cell} value.
- $E^\circ_{\text{cell}} = E^\circ_{\text{red}} + E^\circ_{\text{ox}}$

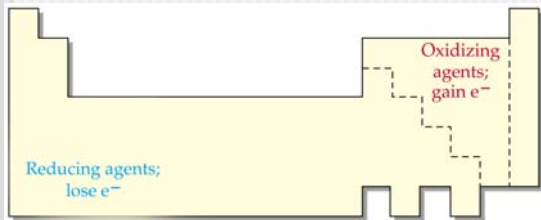
Cell Potentials

- $\text{F}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{F}^-(\text{aq}) \quad E^\circ_{\text{red}} = 2.87 \text{ V}$
- This is the most positive E°_{red} value.
Makes sense - F is most electronegative element and really wants to gain an electron (be reduced, or act as oxidizing agent).

Cell Potentials

- $\text{Li}^+(\text{aq}) + \text{e}^- \rightarrow \text{Li}(\text{s}) \quad E^\circ_{\text{red}} = -3.04 \text{ V}$
- This is the most negative E°_{red} value.
Does this make sense?
- Li is going to lose an electron and be oxidized. This makes it a good reducing agent.

Oxidizing/Reducing Agents



Cell Potentials

- Based on their E°_{red} values, determine the best oxidizing agent, worst oxidizing agent, best reducing agent, and worst reducing agent.
- $\text{Au}^{3+} + e^{-} \rightarrow \text{Au}(s)$ $E^{\circ}_{\text{red}} = 1.50 \text{ V}$
- $\text{Br}_2(l) + e^{-} \rightarrow 2\text{Br}^{-}(aq)$ $E^{\circ}_{\text{red}} = 1.07 \text{ V}$
- $\text{Pb}^{2+} + e^{-} \rightarrow \text{Pb}(s)$ $E^{\circ}_{\text{red}} = -0.13 \text{ V}$
- $\text{Ni}^{2+} + e^{-} \rightarrow \text{Ni}(s)$ $E^{\circ}_{\text{red}} = -0.25 \text{ V}$

TABLE 10.1 Standard Reduction Potentials at 25°C

Reduction Half-Reaction	E° (V)
$\text{F}_2(g) + 2e^{-} \rightarrow 2\text{F}^{-}(aq)$	2.87
$\text{H}_2\text{O}_2(aq) + 2\text{H}^{+}(aq) + 2e^{-} \rightarrow 2\text{H}_2\text{O}(l)$	1.78
$\text{MnO}_4^{-}(aq) + 8\text{H}^{+}(aq) + 5e^{-} \rightarrow \text{Mn}^{2+}(aq) + 4\text{H}_2\text{O}(l)$	1.51
$\text{Cl}_2(g) + 2e^{-} \rightarrow 2\text{Cl}^{-}(aq)$	1.36
$\text{Cr}_2\text{O}_7^{2-}(aq) + 14\text{H}^{+}(aq) + 6e^{-} \rightarrow 2\text{Cr}^{3+}(aq) + 7\text{H}_2\text{O}(l)$	1.33
$\text{O}_2(g) + 4\text{H}^{+}(aq) + 4e^{-} \rightarrow 2\text{H}_2\text{O}(l)$	1.23
$\text{Br}_2(l) + 2e^{-} \rightarrow 2\text{Br}^{-}(aq)$	1.09
$\text{Ag}^{+}(aq) + e^{-} \rightarrow \text{Ag}(s)$	0.80
$\text{Fe}^{3+}(aq) + e^{-} \rightarrow \text{Fe}^{2+}(aq)$	0.77
$\text{O}_2(g) + 2\text{H}^{+}(aq) + 2e^{-} \rightarrow \text{H}_2\text{O}_2(aq)$	0.70
$\text{I}_2(s) + 2e^{-} \rightarrow 2\text{I}^{-}(aq)$	0.54
$\text{O}_2(g) + 2\text{H}_2\text{O}(l) + 4e^{-} \rightarrow 4\text{OH}^{-}(aq)$	0.40
$\text{Cu}^{2+}(aq) + 2e^{-} \rightarrow \text{Cu}(s)$	0.34
$\text{Sn}^{4+}(aq) + 2e^{-} \rightarrow \text{Sn}^{2+}(aq)$	0.15
$2\text{H}^{+}(aq) + 2e^{-} \rightarrow \text{H}_2(g)$	0
$\text{Pb}^{2+}(aq) + 2e^{-} \rightarrow \text{Pb}(s)$	-0.13
$\text{Ni}^{2+}(aq) + 2e^{-} \rightarrow \text{Ni}(s)$	-0.26
$\text{Cd}^{2+}(aq) + 2e^{-} \rightarrow \text{Cd}(s)$	-0.40
$\text{Fe}^{2+}(aq) + 2e^{-} \rightarrow \text{Fe}(s)$	-0.45
$\text{Zn}^{2+}(aq) + 2e^{-} \rightarrow \text{Zn}(s)$	-0.76
$2\text{H}_2\text{O}(l) + 2e^{-} \rightarrow \text{H}_2(g) + 2\text{OH}^{-}(aq)$	-0.83
$\text{Al}^{3+}(aq) + 3e^{-} \rightarrow \text{Al}(s)$	-1.66
$\text{Mg}^{2+}(aq) + 2e^{-} \rightarrow \text{Mg}(s)$	-2.37
$\text{Na}^{+}(aq) + e^{-} \rightarrow \text{Na}(s)$	-2.71
$\text{Li}^{+}(aq) + e^{-} \rightarrow \text{Li}(s)$	-3.04

Cell Potentials

- Ni(s) is the easiest to oxidize, best reducing agent.
- Au(s) is the hardest to oxidize, worst reducing agent.
- Ni²⁺ is the hardest to reduce, worst oxidizing agent.
- Au³⁺ is the easiest to reduce, best oxidizing agent.

Cell Potentials in Reactions

- What will E°_{cell} be if we react Ni(s) with Au³⁺?
- $E^\circ_{\text{ox}} \text{Ni(s)} = +0.25\text{V}$, $E^\circ_{\text{red}} \text{Au}^{3+} = 1.50\text{V}$
- $E^\circ_{\text{cell}} = +0.25\text{V} + 1.50\text{V} = 1.75\text{V}$
- What will E°_{cell} be if Pb²⁺ reacts with Br?
- $E^\circ_{\text{cell}} = -1.07\text{V} + -0.13\text{V} = -1.20\text{V}$
- Not a spontaneous reaction.

Cell Potentials of Reactions

- What combination of 2 reactions will yield the most positive E°_{cell} ?
- Au³⁺ + Ni(s)
- Worked Example 17.4, 17.5; Problems 17.7 - 17.9

Example: $\text{Cl}_2(\text{g}) + \text{Zn}(\text{s})$

- What combination of 2 reactions will yield the most positive E°_{cell} ?
- $\text{Cl}_2(\text{g}) + 2 \text{e}^- \rightarrow 2 \text{Cl}^-(\text{aq}) \quad E^\circ_{\text{red}} = 1.36 \text{ V}$
- $\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Zn}(\text{s}) \quad E^\circ_{\text{red}} = -0.76 \text{ V}$
- The first reaction is a stronger oxidizing agent than the second reaction. Therefore it wants to be the reduction $\frac{1}{2}$ reaction and the second reaction wants to be the oxidation $\frac{1}{2}$ reaction.
- $\text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2 \text{e}^- \quad E^\circ_{\text{ox}} = +0.76 \text{ V}$
- The E°_{ox} reaction is flipped so the sign is flipped!
 - (Zn^{2+} is a weak oxidizing agent, Zn is a strong reducing agent!)

E°_{cell} , K , and ΔG°

- $\Delta G^\circ = -nFE^\circ$
 - n = number of electrons transferred (from the overall balanced cell reaction)
 - F = Faraday's constant: $96,500 \text{ J/V} \cdot \text{mol e}^-$
 - E = cell potential of the reaction
- $\Delta G = \Delta G^\circ + RT \ln K$ (not standard state)
- $-nFE = -nFE^\circ + RT \ln K$
- $E = E^\circ_{\text{cell}} - (RT/nF) \ln K$

Cell Potential Equations

- $E = E^\circ_{\text{cell}} - (2.303 RT) / nF \log K$
(correction between \ln and \log)
- $E = E^\circ_{\text{cell}} - (0.0592 \text{ V}) / n \log K$ (at 25°C)
 - This only applies if all solutions aren't 1 molar. Then it is non-standard.
- $E^\circ_{\text{cell}} = (RT / nF) (\ln K)$ (At equilibrium)
 - $R = 8.314 \text{ J/mol} \cdot \text{K}$
- If we know one of these values, we can find the other two.

Calculations

- Write the half reactions and balanced net reaction
- Find the E°_{red} values, find E°_{ox} values
- Calculate ΔG°
 - $\Delta G^\circ = -nFE^\circ$
- Calculate K
 - $E^\circ = (RT/nF) \ln K$

Calculations

- Calculate ΔG° for the $\text{Ni(s)} + \text{Au}^{3+}$ reaction.
 - $E^\circ_{\text{cell}} = 1.75 \text{ V}$, 6 mol e^- transferred
 - $\Delta G^\circ = -(6 \text{ mol } e^-)(96,500 \text{ J/V}\cdot\text{mol } e^-)(1.75 \text{ V})$
 $= -1.01 \times 10^4 \text{ kJ}$
- Calculate K for this cell at 25°C:
- $\text{Ni(s)} \mid \text{Ni}^{2+}(\text{aq}) \parallel \text{Br}^-(\text{aq}) \mid \text{Pt(s)}$

Cell Potentials Summary

- Large values of K: product-favored reaction
 - ΔG° is negative, E°_{cell} is positive
- Small values of K; reactant-favored reaction
 - ΔG° is positive, E°_{cell} is negative
- Worked Example 17.3

The Nernst Equation

- $E = E^{\circ}_{\text{cell}} - (RT/nF) \ln Q$
- At equilibrium, $E = 0$ and $Q = K$
- $E^{\circ}_{\text{cell}} = RT/nF \ln K$
- Calculate the cell potential if $[\text{Pb}(\text{NO}_3)_2] = 0.88 \text{ M}$ and $[\text{Ag}(\text{NO}_3)] = 0.14 \text{ M}$
- Write the half-reactions for this cell. Write the short-hand notation of this reaction and draw the galvanic cell.
- Examples 17.6 - 17.7, Problem 17.10 - 17.11

Pb and Ag Galvanic Cell

- $2\text{Ag}^+(\text{aq}) + \text{Pb}(\text{s}) \rightarrow 2\text{Ag}(\text{s}) + \text{Pb}^{2+}(\text{aq})$
- $E^{\circ}_{\text{cell}} = 0.13 \text{ V} + 0.80 \text{ V} = 0.93 \text{ V}$
- $Q = (0.88 \text{ M}) / (0.14 \text{ M})^2 = 44.9$
- $E = E^{\circ} - (RT/nF) \ln Q$
- $E = 0.93 \text{ V} - [(8.314 \text{ J/mol K} \cdot 298 \text{ K}) / (2 \text{ mol e}^- \cdot 96,500 \text{ J/V mol e}^-)] \cdot ??$

Corrosion

- The oxidative deterioration of a metal (i.e., solid metal converted to ions).
- Rust formation is the corrosion of iron.
- Metals can be plated with non-reactive metals (chromium, tin, or zinc are common)

Electrolysis

[sample electrolytic cell](#)

[Electroplating movie](#)

- Electrolytic Cell: Electrical energy from an external source (outlet or a battery) is used to force a redox reaction to go in the nonspontaneous direction.
- Molten salt: $2\text{NaCl}(l) \rightarrow 2\text{Na}(s) + \text{Cl}_2(g)$
- $E_{\text{cell}} = -4 \text{ V}$
- This reaction naturally wants to run in reverse direction. We need more than 4 volts to drive this reaction forward. Salts don't normally decompose into elements.

Electrolysis of Water

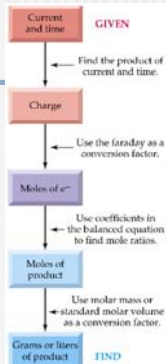
- Water doesn't naturally decompose into hydrogen and oxygen.
- $2\text{H}_2\text{O}(l) \rightarrow 2\text{H}_2(g) + \text{O}_2(g)$ $E_{\text{cell}} = -1.23 \text{ V}$

Anode: $2\text{H}_2\text{O}(l) \rightarrow \text{O}_2(g) + 4\text{H}^+(aq) + 4e^-$

Cathode: $4\text{H}_2\text{O}(l) + 4e^- \rightarrow 2\text{H}_2(g) + 4\text{OH}^-(aq)$

Electrolysis Calcs.

- Used to find mass or volume of product produced by passing current through cell.
- Current: measured in Amps ($A = C/s$).
- Change time to seconds.
- Convert to moles (use F)

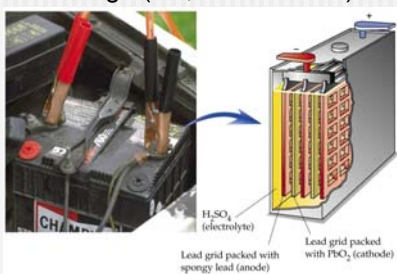


Electrolysis Calculations

- How many grams of copper can be collected in 1.00 hour by a current of 1.62 A from a CuSO_4 solution?
- $\text{Current (C/s)} \times \text{time (s)} = \text{C}$
- $\text{C} \times (1 \text{ mol } e^- / 96,500 \text{ C}) = \text{mol } e^-$
- $\text{mol } e^- \times (\text{mol solid} / \text{mol } e^-) = \text{mol solid}$
- $\text{mol solid} \times (\text{molar mass}) = \text{mass solid}$
- $3600 \text{ sec} (1.62 \text{ C / sec}) (1 \text{ mol } e^- / 96,500 \text{ C}) (1 \text{ mol Cu} / 2 \text{ mol } e^-) (63.5 \text{ g/mol}) = 1.92 \text{ g Cu}$

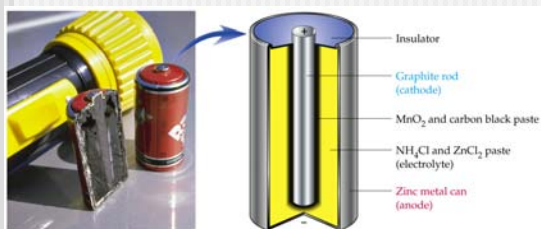
Batteries

- Lead storage (i.e., car batteries)

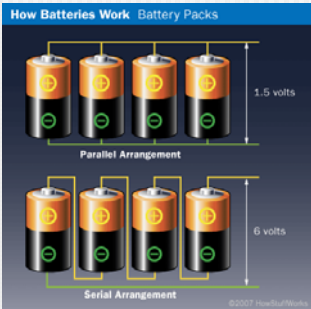


Household batteries

- Dry-cell (or Laclanche) batteries



9V battery – sum of 1.5 Volts

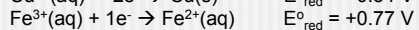
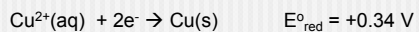
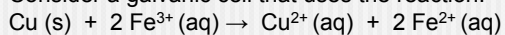


Ni-Cad Batteries - rechargeable

Lithium Batteries

Group Quiz

Consider a galvanic cell that uses the reaction:



What is the potential of a cell at 25°C that has the following ion concentrations?

$$[\text{Fe}^{3+}] = 1.0 \times 10^{-4} \text{ M} \quad [\text{Cu}^{2+}] = 0.25 \text{ M}$$

$$[\text{Fe}^{2+}] = 0.20 \text{ M}$$

What is the anode? The cathode? Draw the cell.

The End
