Oxidation and Reduction

- When an element loses an electron, the process is called oxidation:

  $Na(s) \rightarrow Na^+(aq) + e^-$

- The net charge on an atom is called its oxidation state—in this case, Na(s) has an oxidation number of 0, and $Na^+(aq)$ has an oxidation number of +1
- Oxidation corresponds to an increase in the oxidation number

Oxidation and Reduction

- Examples of oxidation:

$Ag(s) \rightarrow Ag^+(aq) + e^-$

0 +1

$2FeO(s) + O_2(g) \rightarrow Fe_2O_3(s) + 2e^-$

+2 -2 0 +3 -2

$Mn^{2+} + 12H_2O \rightarrow MnO_4^- + 8H_3O^+ + 5e^-$

+2 +1 -2 +7 -2 +1 -2

Oxidation numbers of atoms shown in blue

Oxidation and Reduction

- When an element gains an electron, the process is called reduction:

  $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$

- In this case, $Cl_2(g)$ has an oxidation number of 0, and $Cl^-(aq)$ has an oxidation number of -1
- Reduction corresponds to a decrease in the oxidation number

Oxidation and Reduction

- Examples of reduction:

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

+2 0

$O_2(g) + 4H_3O^+(aq) + 4e^- \rightarrow 6H_2O(\lambda)$

0 +1 -2 +1 -2

$MnO_4^- + 4H_3O^+ + 2e^- \rightarrow Mn^{2+} + 6H_2O$

+7 -2 +1 -2 +2 +1 -2

Oxidation numbers of atoms shown in blue

Oxidation and Reduction

- An oxidation or reduction reaction, as shown in the previous slides, is called a half-reaction
- Two half reactions are combined to form an electrochemical reaction

$$2x\ \ (Na(s) \rightarrow Na^+(aq) + e^-)\ \ \text{oxidation}$$

$$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)\ \ \text{reduction}$$

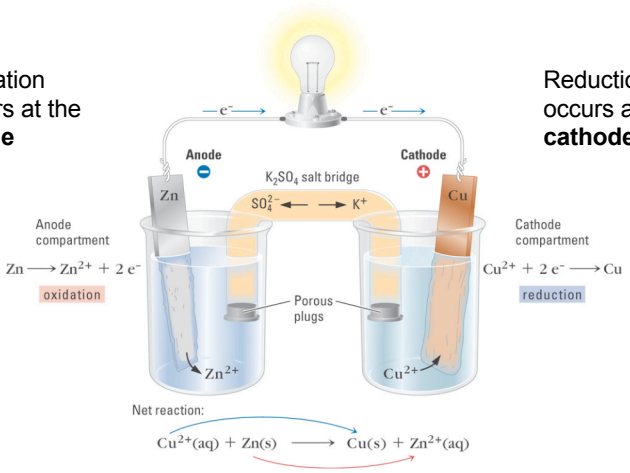
$$\text{net:}\quad 2Na(s) + Cl_2(g) \rightarrow 2Na^+ + 2Cl^-$$

Oxidation and Reduction

- When combining half reactions, one must be an oxidation reaction, and the other must be a reduction reaction because the electrons freed in the oxidation step are then used in the reduction step
- An electrochemical cell results when two half reactions are combined

Electrochemical Cells

Oxidation occurs at the **anode**



Reduction occurs at the **cathode**

Figure 19.3

Electrochemical Cells

- Each half reaction has an electrical potential, E
- Electrical potential is a measure of how easily a species is reduced
  - e⁻'s added to the species to reduce its oxidation state
- The emf (electromotive force) of a cell is a measure of how much work that cell can do

Electrochemical Cells

- The emf of a cell is determined by taking the difference between the potentials of the cathode and the anode:

  $E_{cell} = E_{cathode} - E_{anode}$

- If E_{cell} is positive the electrochemical reaction will proceed as written
- If E_{cell} is negative, the reverse reaction will occur

Electrochemical Cells

- Values for the potential of various half reactions can be found in tables
- Tables are usually given as standard reduction potentials, E^o
  - All half reactions are written as reduction reactions
  - To write an oxidation reaction, simply flip the reactants and products and change the sign on E^o

Electrochemical Cells

Examples:

$Co^{3+}(aq) + e^- \rightarrow Co^{2+}(aq)$ $E^o = 1.82$ V

$Au^{3+}(aq) + 3\ e^- \rightarrow Au(s)$ $E^o = 1.50$ V

$Hg_2^{2+}(aq) + 2\ e^- \rightarrow 2\ Hg(\lambda)$ $E^o = .789$ V

$I_2(s) + 2\ e^- \rightarrow 2\ I^-(aq)$ $E^o = .535$ V

$2\ H_3O^+(aq) + 2\ e^- \rightarrow H_2(g) + 2\ H_2O$ $E^o = 0.000$ V

$PbSO_4(s) + 2\ e^- \rightarrow Pb(s) + SO_4^{2-}(aq)$ $E^o = -.356$ V

$Cd^{2+}(aq) + 2\ e^- \rightarrow Cd(s)$ $E^o = -.403$ V

$Li^+(aq) + e^- \rightarrow Li(s)$ $E^o = -3.045$ V

Lead-Salt Battery

Car battery electrochemistry:

$Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$ (oxidation)

0 +2

$PbO_2 + 4H_3O^+ + SO_4^{2-} + 2e^- \rightarrow$

+4 -2

$PbSO_4 + 6H_2O$ (reduction)

+2

Net: $Pb + PbO_2 + 2SO_4^{2-} + 4H_3O^+ \rightarrow$

$2PbSO_4 + 6H_2O$ $E^o = 2.04$ V

Lead-Salt battery

- When you start your car, you draw electrical power from the battery using the electrochemical reaction on the previous slide
- Once your car has started, the alternator reverses the voltage on the battery so the reverse electrochemical reaction occurs—recharges battery

Fuel Cells

- Fuel cells are hailed by many as the technology of the future for automotive engines because they do not release any pollutants into the atmosphere
- Fuel cells are electrochemical cells that convert chemical energy into electrical power

Fuel Cells

Proton Exchange Membrane Fuel Cell

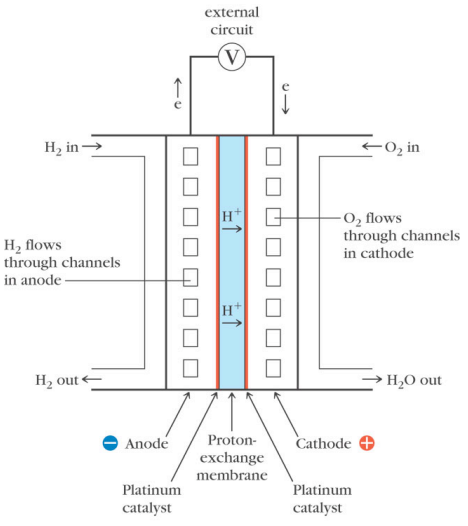
$H_2 \rightarrow 2H^+ + 2e^-$ (oxid)

$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$ (reduct)

Net reaction:

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

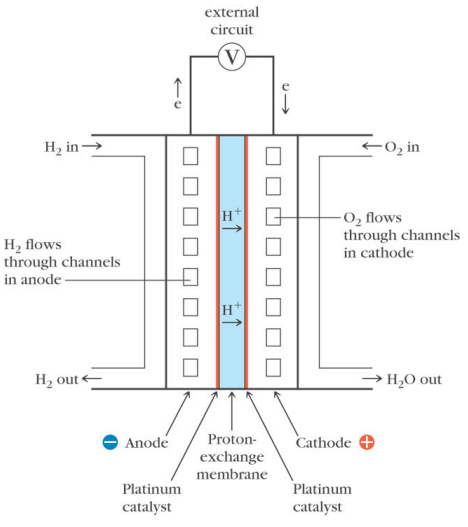
$E \approx 0.7$ V



Fuel Cells

The problem with the proton exchange membrane fuel cell is the storage and transportation of hydrogen (remember the Hindenburg)

Most research is currently working on different ways to generate H_2 from safer starting materials



Fuel Cells

Some options include:

- CH_4 + catalyst → H_2 + CO_2
  - Based on natural gas; readily available; known storage & handling
- $NaBH_4$ + catalyst → H_2 + $Na_2B_4O_7 \cdot 10H_2O$ (borax)
  - Solid material; easy storage and transport; by-product has industrial uses