Paper Three: Topic C. Energy Sources
DP Chemistry Ann Arbor Huron H.S.

I. What makes a good energy source?:

Vocabulary:
efficient, controlled, waste is benign, extraction, processing, transportation, power plant efficiency, transmission

$$\text{Efficiency of Transfer} = \frac{\text{Useful output E}}{\text{Total Input E}} \times 100$$

$$\text{Energy Density} = \frac{\text{Energy released from fuel}}{\text{Volume of fuel consumed}}$$

$$\text{Specific Energy} = \frac{\text{Energy released from fuel}}{\text{Mass of fuel consumed}}$$

EX 1: Calculate the energy density of coal (carbon) in kJ per cubic meter.
The ΔH° of coal combustion is -394 kJ/mol. Coal has a density of 2267 kg/m^3.

Renewable Energy Sources vs Non-Renewable:

Renewable

Non-renewable

Ex 2: Why is ethanol produced from fermenting corn considered renewable, even though it releases CO_2?

II. The Origin of all Fossil Fuels

Vocabulary:
photosynthesis, carbon reduction vs oxidation, coal, gas, crude oil, fractional distillation, thermal cracking

Ex 3: A C_{15} alkane is heated over a catalyst and chemically cracked into ethene, propene, and octane.
Deduce a balanced equation for this cracking reaction.

Auto ignition "knocking" and the octane number:

Pure 2,2,4-trimethylpentane has an octane number of 100. It is higher than aliphatic octane. Heptane has an octane number of zero. If a car burns fuel at 87 octane it is the equivalent of 87% 2,2,4-trimethylpentane and 13% heptane. More branched alkanes resist combusting during the compression step in an automobile cylinder.

Octane ratings decrease with increased carbon chain (hexane > heptane). Rings and branches have higher octane ratings that do aliphatics.

Ex 4:

Rank the following three chemicals according to octane content: 2-methylpentane, benzene, hexane

Catalytic Reforming:

Using catalysts to convert aliphatic alkanes into branched or ring structures with higher octane ratings.

Ex 5:

Show the reformation reaction of hexane to 2,2-dimethylbutane using a Pt catalyst and zeolite.

Show the reformation reaction of heptane to methylbenzene using Pt catalyst and aluminum oxide.

Greener ways to use fossil fuels:

AIM	EXAMPLES	ADVANTAGES
Remove sulfur from fuel	Scrubbing, filters, engineered polymers with chemical receptors for sulfur	Reduces SO_2 emissions which lead to acid rain. Extracted sulfur can be reclaimed.
Produce fuels with lower environmental impact	Remove, Hg, Pb, S, benzene. Use catalytic converters	Reduces CO, NO_x, SO_2, lead and mercury oxides
Produce alternative or blended petrol	Add ethanol to gasoline, use compressed natural gas	Reduces overall CO, CO_2 and NO_x release
Develop renewable and alternatives	Bioethanol, biodiesel, biogas, electric cars, hybrid cars, fuel cells	Reduce dependence on oil, C-neutral biofuels (absorb CO_2 as they form)

Coal Gasification:

There is more coal that there is oil. Use steam and oxygen to turn carbon into hydrocarbons. Can be done underground with low industrial costs. Also produces a clean gas with few impurities (filtered). Byproducts can be used as fertilizer.

Coal Liquefaction:

Take coal gas, compress it add water and CO_2 and a catalyst. Create a low impurity liquid hydrocarbon.

Carbon Capture and Storage (CCS):

Capture carbon dioxide from large industrial sources, compress it, inject it underground and cap it so as to keep it from re-entering the environment. Usually stored in porous sandstone.

Carbon Footprint:
The amount CO_2 released when a fuel is combusted. Biofuels cost more, but have lower carbon footprints due to the fact that they absorb CO_2 from the atmosphere via photosynthesis.

III. Nuclear Fusion and Fission:

Fusion: To connect objects together. Product's mass increases.
One could fuse two pieces of metal together.
Fission: To split an object into pieces. Products have lower mass.
As the tectonic plates of Earth separated, a fissure was formed.

Fusion of Hydrogen nuclei to form Helium. This occurs in the sun.

Pros: Fuel is abundant and the byproducts are non-toxic. Helium is in short supply.

Cons: Takes a ridiculous amount of energy to initiate and no material can contain it.

$E = mc^2$ (known as mass defect):
Helium is made from 2 protons and 2 neutrons yet the mass is less than this (not conserved). The defect in mass can be explained as being converted directly into energy. This is also true with fission.

Ex 6:
A proton has a rest mass of 1.672622×10^{-27} kg, a neutron has a rest mass of 1.674927×10^{-27} kg. The helium nucleus has a rest mass of 6.64477×10^{-27} kg. Use the mass of two protons and two neutrons to calculate the mass defect of the helium nucleus.

Nuclear Binding Energy:
The energy required (+) to separate a nucleus into its constituent parts (p+ and n°).
As with all things thermodynamic, this could also be seen as the energy released when the constituent parts reform. (-) These energies are massive compared to the enthalpy of bonds. Remember, the nuclear strong force holds the nucleus together. It has a relative force of 1.0. The electrostatic force (the one involved in bonding) is 1/137 of the nuclear strong force!

The nuclear binding energy in a helium nucleus is much greater than those in the hydrogen isotopes used as reactants. Hence the large energy release and mass defect.

Possible Fusion Reactions:

$${}^{2}_{1}H + {}^{3}_{1}H \rightarrow {}^{4}_{2}He + {}^{1}_{0}n + \text{Energy}$$

Deuterium and Tritium fuse to form Helium and the release of a neutron.

Chain Reaction:
A self-sustaining reaction. A product of the reaction initiates the second or more following reactions.
The combustion of hydrocarbons is a chemical example of this. The heat released during combustion serves as activation energy for the following reactions.

Nuclear Fission:

$$^{235}_{92}U + ^{1}_{0}n \rightarrow ^{141}_{56}Ba + ^{92}_{36}Kr + 3\,^{1}_{0}n$$

The three neutrons can serve to initiate three more nuclear events. (nuclear chain reaction)

In nuclear power plants the fuel is separated into rods and surrounded by a moderator. A moderator is a substance that absorbs or deflects neutrons so that the chain reaction does not break away or become out of control (a nuclear melt down). All elements with an atomic mass greater than 92 are considered transuranium elements and can undergo fission.

<u>Critical Mass:</u> The amount of fissionable material needed to carry out a sustained chain reaction is referred to as critical mass.

<u>Critical Reactor</u>: when the number of neutrons released in one generation is equal to the amount of neutrons released in the next generation.
<u>Supercritical Reactor</u>: when the number of neutrons released in successive generations is increasing. Power output increases and the control rods get used up to absorb neutrons to avoid meltdown.
<u>Subcritical Reactor</u>: when the number of neutrons released in successive generations is decreasing. This reactor is no longer self-sustaining.

<u>Transmutation</u>: The conversion from one element to another by capture or emission of a particle.

Name	Symbol(s)	Representation	Description
Alpha particle	$^{4}_{2}He$ or $^{4}_{2}\alpha$		(High-energy) helium nuclei consisting of two protons and two neutrons
Beta particle	$^{0}_{-1}e$ or $^{0}_{-1}\beta$		(High-energy) electrons
Positron	$^{0}_{+1}e$ or $^{0}_{+1}\beta$		Particles with the same mass as an electron but with 1 unit of positive charge
Proton	$^{1}_{1}H$ or $^{1}_{1}p$		Nuclei of hydrogen atoms
Neutron	$^{1}_{0}n$		Particles with a mass approximately equal to that of a proton but with no charge
Gamma ray	γ		Very high-energy electromagnetic radiation

Ex 7:
Write an equation for the transmutation by proton capture followed by the alpha decay of Pa-237.

Types of Nuclear Decay:

Alpha Emission: ${}^{4}_{2}\alpha$ In alpha decay, the nucleus emits a particle that has the same constitution as a helium nucleus, with 2 protons and 2 neutrons.

$${}^{4}_{2}\alpha = {}^{4}_{2}He$$

When a nucleus undergoes alpha decay:
- Subtract 4 from the mass #.
- Subtract 2 from the atomic #.

$${}^{238}_{92}U \rightarrow {}^{4}_{2}\alpha + {}^{234}_{90}Th$$

(remember, Thorium is identified by its atomic #, 90)

Beta Emission: ${}^{0}_{-1}\beta$ A beta particle is identical to an electron. In beta decay, the nucleus changes a neutron into a proton and an electron and emits the electron.

$${}^{1}_{0}n \rightarrow {}^{0}_{-1}\beta + {}^{1}_{1}p$$

When a nucleus undergoes beta decay:
- The mass # remains the same.
- Add 1 to the atomic #.

$${}^{14}_{6}C \rightarrow {}^{0}_{-1}\beta + {}^{14}_{7}N$$

Positron Emission: ${}^{0}_{+1}\beta$ A positron is like an electron with a positive charge. In positron emission, the nucleus changes a proton into a neutron and a positron, and emits the positron.

$${}^{1}_{1}p \rightarrow {}^{0}_{+1}\beta + {}^{1}_{0}n$$

When a nucleus undergoes positron emission:
- The mass number remains the same.
- Subtract one from the atomic number.

$${}^{8}_{5}B \rightarrow {}^{0}_{+1}\beta + {}^{8}_{4}Be$$

Electron Capture: ${}^{0}_{-1}e'$ In electron capture, the nucleus captures a low energy electron and combines it with a proton to form a neutron.

$${}^{0}_{-1}e' + {}^{1}_{1}p \rightarrow {}^{1}_{0}n$$

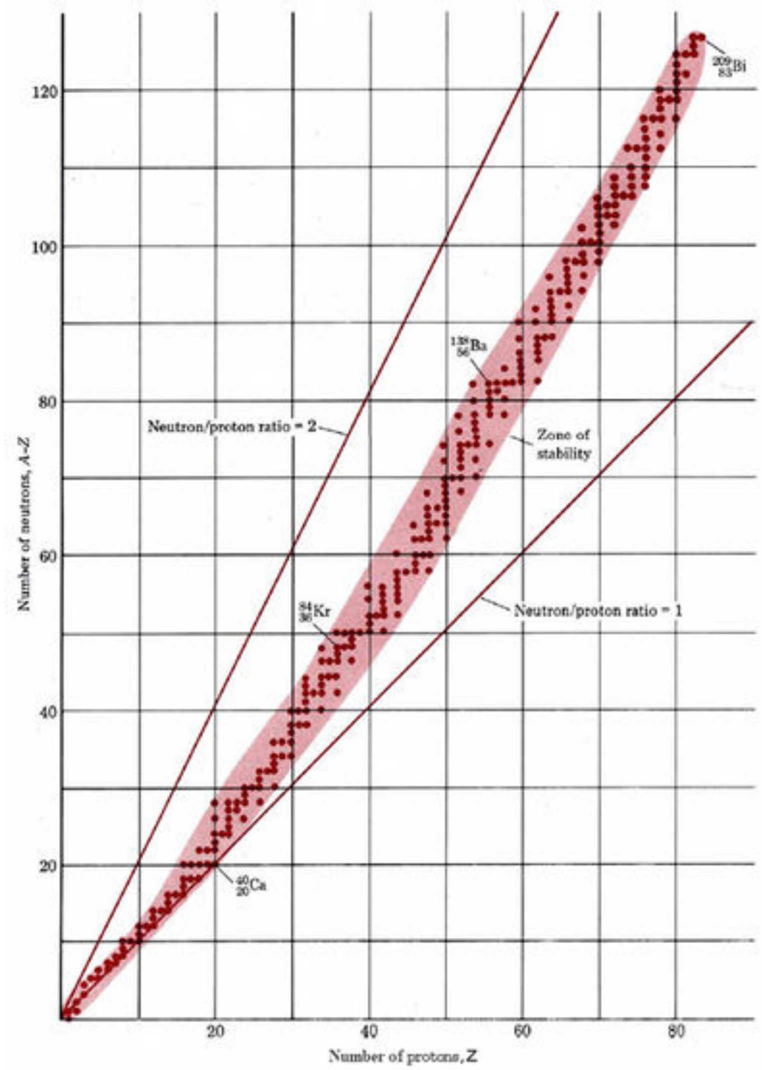
When a nucleus undergoes electron capture:

- The mass number remains the same.
- Subtract 1 from the atomic number

$${}^{18}_{9}F + {}^{0}_{-1}e' \rightarrow {}^{18}_{8}O$$

Gamma Rays: ${}^{0}_{0}\gamma$ Gamma rays are electromagnetic radiation and have no mass and no charge. Gamma rays usually accompany other forms of nuclear decay. They can be emitted in nuclear fission and in nuclear fusion.

Nuclear stability is based on proton/neutron ratios



Nuclei undergo decay to achieve greater stability. You can use the previous chart to predict the kind of decay an isotope will undergo. If we plot the number of neutrons against the number of protons for all known stable (i.e., nonradioactive) nuclei, we obtain the result shown previously. All the stable nuclei lie within a definite area called the **zone of stability**. For low atomic numbers, most stable nuclei have a neutron/proton ratio which is very close to 1. As the atomic number increases, the zone of stability corresponds to a gradually increasing neutron/proton ratio. In the case of the heaviest stable isotope, $^{209}Bi_{83}$ for instance, the neutron/proton ratio is 1.518. If an unstable isotope lies to the left of the zone of stability, it is neutron rich and decays by β emission. If it lies to the right of the zone, it is proton rich and decays by positron emission or electron capture.

Alpha decay is seen mainly in very large nuclei, usually with atomic numbers of 83 or greater.

Half-Life

The half-life of a radioactive substance is the time it takes for half of the substance to decay. Most half-life problems can be solved by using a simple chart. A sample with a mass of 120 grams and a half-life of 3 years will decay as follows. Don't forget that the chart should start with time at zero.

HALF LIVES	TIME	SAMPLE	AMOUNT REMAINING	FRACTION REMAINING
0	0 years	120 g	100%	1
1 half-life	3 years	60 g	50%	1/2
2 half-life	6 years	30 g	25%	1/4
3 half-life	9 years	15 g	12.5%	1/8
4 half-life	12 years	7.5 g	6.25%	1/16
5 half-life	15 years	3.75 g	3.125%	1/32

Remember, most radioactive decay is first order overall. The half-life equation is:

$$\mathbf{t_{1/2} = \ln 2/k}$$

The rate of decay is constant (not concentration dependent) and therefore radioactive elements are used in dating approximations with small levels of uncertainty. If you know starting and ending amounts you can use this rate law:

$$\mathbf{\ln[A]_t = -kt + \ln[A]_\circ}$$

Uranium Enrichment:

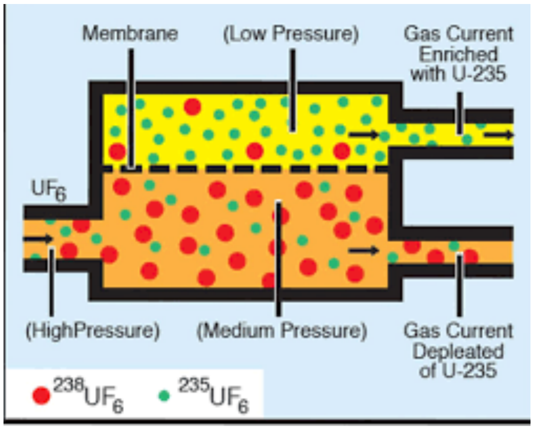
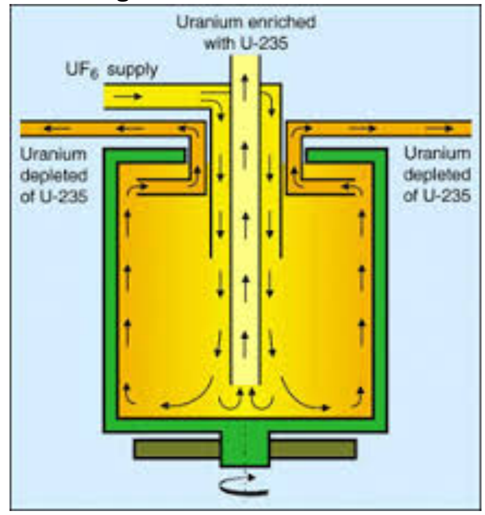
1.0 gram of enriched U-235 can produce 310 gigajoules of energy via fission.
This is equivalent to 140,000 kg of coal, or 93,000 liters of gasoline. This reaction releases no CO_2.

Unfortunately, only 0.7% of the uranium on Earth is U-235. The remaining 99.3% is U-238.
Uranium ore contains two isotopes of UO_2. Since UO_2 melts at 2800 °F it is not energy efficient to vaporize the UO_2. Instead the Uranium is converted to UF_6 via the following process:

UO_2 (s) + 4HF (aq) $\rightarrow$ UF_4 (s) + $2H_2O$ (g)

UF_4 (s) + F_2 (g) $\rightarrow$ UF_6 (g)

$UF_{6\,(235)}$ and $UF_{6\,(238)}$ can be separated by effusion or centrifugation.

Effusion:	Centrifugation:
	

Mathematically the rates of separation can be determined via Graham's Law of Effusion.

KE (UF_6- $_{235}$) = KE (UF_6- $_{238}$) or $1/2mv^2$ (UF_6- $_{235}$) = $1/2mv^2$ (UF_6- $_{238}$)

Ultimately:

$$\frac{R1}{R2} = \frac{\sqrt{(M2)}}{\sqrt{(M1)}}$$

Radioactive Waste: Uranium reactors utilizing UF_6- $_{235}$ can produce electricity when the UF_6- $_{235}$ reaches 20%. UF_6- $_{235}$ must be 85+% to be used as a weapon. The ionizing radiation emitted from the daughter products is of great concern. This ionizing radiation can cause cell damage such as cancer or radiation sickness.

Ionizing radiation is measured using the SI unit, Sieverts (Sv). It measures the ionizing radiation effect in J/kg. The background level of radiation is 2.4 mSv/year. 250 mSv can be detected by blood tests. A blood level of 1.0 Sv (1000 mSv) will display effects of radiation poisoning, such as nausea, headaches and vomiting.

In your body, ionizing radiation can produce free radicals by removing electrons from molecules. The radicals, superoxide, $\cdot O_2^-$ and Hydroxyl, HO· can damage DNA and enzymes.

Discuss the consequences of nuclear waste and disposal.

IV. Solar Energy and its Roll in Biofuels

Photosynthesis:

The conjugated double bonds (alternating single and double bonds) in the plant's pigments allow for the light's energy to be absorbed. This absorption excites electrons. When the electrons return to their ground state this released energy initiates a complex series of reactions that result in the following overall reaction:

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$$

All fossil fuels and foods have been formed by using solar energy to transform carbon dioxide into carbon containing substrates.

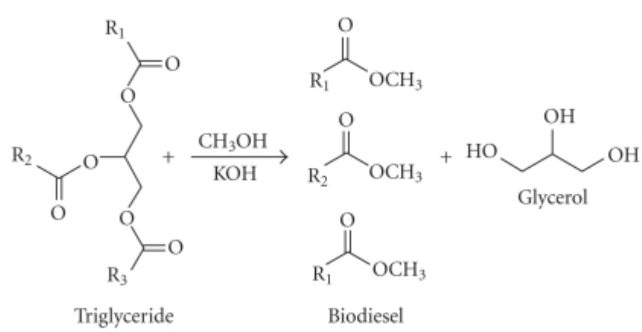
<u>Biofuels:</u>

<u>Ethanol:</u> can be produce by fermenting glucose. The ethanol can be combined with petroleum fuel. The ethanol is considered carbon neutral because the glucose is from a plant. As the plant lived, it absorbed carbon dioxide from the atmosphere to turn into glucose.

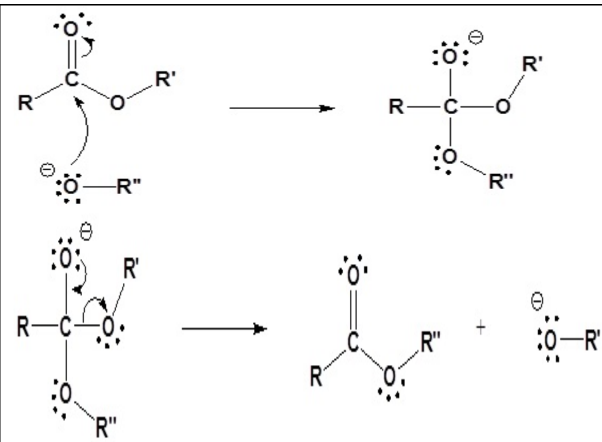
$$C_6H_{12}O_6 \rightarrow 2CH_3CH_2OH + 2CO_2$$

<u>Biodiesel:</u> vegetable oils produce similar energies of combustion as does diesel fuel. They are too viscous to burn in engines. They are also not volatile enough to ignite. One method is to convert long carbon chain esters in oil into shorter carbon chain esters using <u>transesterification</u>. The shorter chains have lower IMF and this makes them more volatile and less viscous.

Transesterification reaction



Transesterification mechanism



Assume R'' is much shorter than R'

<u>Pros and Cons when comparing biodiesel to petroleum diesel</u>:

<u>Pros:</u>

sustainable, a better solvent (cleans engines), lower carbon footprint, less flammable, biodegradable if spilled.

<u>Cons:</u>

more viscous that pet diesel (requires fuel heaters), slightly lower energy of combustion, more expensive, contains nitrogen which can form NOx, competes with food (makes food cost more $).

<u>V. Global Warming:</u>

<u>Greenhouse Effect:</u>

When radiation from the sun reaches Earth, it is absorbed and it releases longer wavelength infrared radiation as it reflects back out to space. <u>Greenhouse gases</u> in the atmosphere absorb this IR radiation and re-radiate it, warming the atmosphere. It is the covalent bonds in greenhouse gases that have resonance frequencies in the

IR region. C-H, C=O, and O-H bonds will vibrate and stretch when exposed to IR radiation. This will cause the dipole moment of the molecule to become distorted. This allows it to be detected in IR spectrophotometry and to view these gases with satellite technology.

Natural Greenhouse Gases:
Natural CO_2 and NO_x are emitted from volcanism. Methane (CH_4) is produced in swamps and in the melting permafrost. 95% of the natural greenhouse gases come from atmospheric water vapor (H_2O). This is a physical equilibrium between the liquid/vapor states. Higher temperatures push the equilibrium state towards that of water vapor, accelerating the atmospheric content of greenhouse gases. The water vapor content on Earth is very stable.

Things that Dim or Cool the Earth: certain chemicals and structures reflect the sun's radiation back to space. Smoke, aerosol-type suspensions from volcanism (H_2SO_4, SO_2, SO_3) and clouds reflect this radiation. When soot and smoke enters clouds, the particles create condensation nuclei. These condensed droplets are effective at reflecting E/M radiation back to space. 2-3 % less radiation has reached Earth over the last two decades due to pollution. Not all global dimming has a positive net effect.

- Some of these processes lead to acid rain
- Global dimming results in less water evaporating on Earth. This leads to lower intensity monsoons which many countries rely on for agriculture.
- These pollutants lead to many health problems.

Human Derived Greenhouse Gases:
Combustion releases CO_2 and this makes up 50% of all human derived (anthropogenic) sources. This carbon came from underground and it is released to the atmosphere. The water vapor released during combustion does not significantly alter the water vapor content of the atmosphere.
Industrial processes and automobile effluent releases NO_x. This accounts for 25% of all anthropogenic gases.
Deforestation and agriculture account for the final 25%. Deforestation eliminates photosynthetic plants that would absorb atmospheric CO2. Agricultural processes (decomposing plants) and ruminant animals produce methane (CH_4).

The Absorption of CO_2 by the Oceans:
30% of anthropogenic CO_2 is absorbed by the oceans. The CO_2 content of the oceans has been rising approximately 1% per year since 1990. As you know: $CO_2 + H_2O \rightarrow H_2CO_3$ this acidity has lowered the pH of the ocean by 0.10 pH units since the industrial revolution.

Global Attempts to Control Climate Change:
In 1997 the Kyoto Protocol was established to address carbon trading and credits. This attempted to lower CO_2 release to 93% of that released in 1997. The United States, Russia and China refused to ratify this protocol. They cited potential business losses as their reason to not participate. The IPCC (International Panel on Climate Change) was established to record data supporting the effect of anthropogenic CO_2 and to educate countries on ways to mitigate CO_2 release. The Kyoto Protocol was extended in Qatar in 2012. In 2015 the Paris Agreement was established to educate the European Union and the rest of the world on ways to mitigate CO_2 release.

Carbon Capture Sequestration:
Sequestration is a way to capture or remove CO_2 or SO_2 that would end up in the atmosphere.

- CCS (Carbon Capture and Storage) Use empty geological features to pump CO_2 into the cavity and to cap it.
- Scrubbers on smoke stacks. $CaO + SO_2 \rightarrow CaSO_4 \cdot 2H_2O$ the water comes from combustion.
- Sequestration. $Mg_2SiO_4 + 2CO_2 \rightarrow MgCO_3 + SiO_2$
- Carbon Recycling. Use CO_2 from powerplants to convert to syngas chemically.

Agriculture and Deforestation:
The raising of beef cattle, pigs and dairy products release large amounts of methane (CH_4) and N_2O. (CH_4) is released when animal waste decomposes and ruminant animals ferment their cellulosic food. N_2O is released when fertilizer is applied too heavily. Rotating crops can eliminate the over application of chemical fertilizers.

- CH_4 is 25 X more potent than CO_2 as a greenhouse gas
- N_2O is 300 X more potent than CO_2 as a greenhouse gas

Electrochemistry: Rechargeable Batteries and Fuel Cells:
Background: Batteries are very usable devices as they are methods of storing energy. Energy storage will become more important as we rely more on alternatives, such as solar, wind and tidal energy. Many of these alternatives are harvested in areas with low populations, necessitating expensive energy transport or storage solutions. Rechargeable batteries use lead, cadmium, and nickel. These elements are toxic to the environment. Hydrogen fuel cells allow us to convert chemical energy directly to electricity, but the transportation and storage of hydrogen is very difficult and expensive.

All batteries involve redox reactions where an anode is oxidized (losing electrons) and the cathode is reduced (gaining electrons). Spontaneous redox reactions are always exothermic. The amount of potential to do electrical work (voltage) is determined by the materials used. The mass of the material will determine the weight of the battery. Silver, mass of 108, vs Lithium, mass of 9, both produce the same quantity of electrons.

In the 1790s Luigi Galvani accidentally discovered that two dissimilar metals simultaneously touching the legs of a dead frog caused them to twitch. He deduced that a moist connection between two dissimilar metals caused this. Alessandro Volta doubted the legs had any electrical connection (he was wrong) and he went on to construct the first battery.

Primary Cells: An electrochemical cell in which the electrodes are consumed or the electrolyte in the moist layer is consumed. These are single use batteries that eventually get thrown away. Primary cells are not very effective during high loads (like an electric car). They are effective at releasing small quantities of current over a long time period (like in a smoke detector or remote control).

Secondary Cells: The chemical reaction that produces the voltage can be reversed by hooking it up to an electrical source. Secondary cells can deliver more current and they have a higher rate of discharge. They also have the problem of self-discharge (where the electrons "leak" even if you are not using them).

Lead Acid Batteries: These are secondary cells that are found in cars, storage grids for solar arrays, and in computer backup batteries. In a car the electricity is used to start the car, fire the spark plugs and to run electronics like a fan or the stereo. While driving the mechanical energy is transformed through the alternator to recharge the battery as you drive. This is why if you sit for a while with your engine off, listening to the radio, you may not have enough power to restart your car. Sulfuric acid is used as the electrolyte.

Anode: $Pb (s) + HSO_4- (aq) \rightarrow PbSO_4 (s) + H^+ (aq) + 2e'$

Cathode: $PbO_2 (s) + 3H^+ + HSO_4^- + 2e' \rightarrow PbSO_4 (s) + + 2H_2O (l)$

Overall Cell Reaction:

$$Pb\ (s) + PbO_2\ (s) + 2H^+\ (aq) + 2HSO_4^-\ (aq) \rightarrow 2PbSO_4\ (s) + 2H_2O\ (l)$$

A fully charged battery will have Pb (s) as an anode. A fully discharged battery will have $PbSO_4$ as the anode.

Lithium Ion Batteries:

The anode is pure lithium absorbed into a graphite electrode. The cathode is a lithium cobalt complex ($LiCoO_2$). The lithium atoms are oxidized into lithium ions. Lithium was chosen for its low mass and for the fact that it has the highest negative reduction potential. The electrons flow from the anode to the cathode until the battery is "dead". At this point the battery is recharged by pushing electrons back onto the lithium ions in the electrode. Lithium ion batteries must use gel type electrolytes as the lithium would react violently with water.

Charging Reaction:
$Li^+ + 1e' \rightarrow Li\ (s)$
$LiCoO_2\ (s) \rightarrow Li^+ + 1e' + CoO_2\ (s)$

Discharging Reaction:
$Li\ (s) \rightarrow Li^+ + 1e'$
$Li^+ + 1e' + CoO_2\ (s) \rightarrow LiCoO_2\ (s)$

Pros (compared to Pb/acid and Ni/Cd): Very high charge density (6 time more energy per kilogram). They hold charge better. They can handle more charge cycles. They contain no heavy metals.

Cons (in general): They are sensitive to high temperatures. They will become damaged if they are completely run flat. They last only about 1000 cycles. They can explode of the separator becomes perforated.

Nickel/Cadmium batteries:

These are an older technology, but they still are the most common type of rechargeable batteries in the D, C, AA, AAA sizes.

Pros: Due to the fact that hydroxide ions are the only ions that are moving, the internal resistance is very low. This allows for quick recharge. They can also be completely drained without damaging the battery.

Cons: They have lower charge densities than Nickel/metal hydride and lithium ion batteries (these are also less toxic).

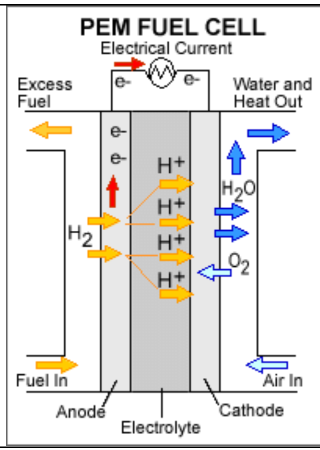
Discharging:
$Cd\ (s) + 2OH^-\ (aq) \rightarrow Cd(OH)_2\ (s) + 2e'$
$2NiO(OH)\ (s) + 2H2O\ (l) + 2e' \rightarrow 2Ni(OH)_2\ (s) + 2OH^-\ (aq)$

Charging:
$Cd(OH)_2\ (s) + 2e' \rightarrow Cd\ (s) + 2OH^-\ (aq)$
$2Ni(OH)_2\ (s) + 2OH^-\ (aq) \rightarrow 2NiO(OH)\ (s) + 2H2O\ (l) + 2e'$

All primary and secondary cells have internal resistance. The amount and charge of the ions that need to move determine this resistance. The surface area of the electrode is also. This resistance is lowered at high temps, but the batteries will discharge at high temps as well. This is why high voltage batteries are often cooled and it is best to store batteries at cool temperatures. The lead/acid batteries in automobiles have great surface are and this is how they can deliver such large amperage for starting an engine.

<u>Hydrogen Fuel Cells:</u>

An electrochemical device that converts chemical potential energy into electrical energy. In a hydrogen fuel cell, hydrogen is the fuel to be oxidized by the oxygen in the air. The byproduct is water so there is no pollution.



Anode: $H_2 \rightarrow 2H^+ + 2e'$.

Cathode: $O_2 + 4e' \rightarrow 2O^{2-}$

Overall Cell Reaction: $2\,H_2 + O_2 \rightarrow 2H_2O$

The PEM is the Proton Exchange Membrane. It allows H+ ions to move through the membrane, forcing the electrons along the conductor. There are also hydrogen fuel cells that are alkaline (OH- is the electrolyte) and cells that are acidic (phosphoric acid is the electrolyte).

<u>Sources of Hydrogen:</u>

Clean Hydrogen: Hydrogen can be produced through electrolysis by using wind or solar to manufacture electricity.

Unclean Hydrogen: Is formed through catalytic reformation of hydrocarbons. Steam and catalysts will be used to turn the hydrocarbons into CO and H_2.

$C_xH_y + xH_2O \rightarrow xCO + (y/2 + x)H_2$

<u>Direct Methanol Fuel Cells:</u>

Methanol is the source of H+ ions at the anode. The PEM is identical to that of a Hydrogen Fuel Cell.

Anode: $CH_3OH + H_2O \rightarrow 6H^+ + 6e' + CO_2$

Cathode: $3/2O_2 + 6H^+ + 6e' \rightarrow 3H_2O$

Cell Reaction: $CH_3OH + 3/2O_2 \rightarrow CO_2 + 2H_2O$

PROS: Requires little water at the anode. Produces a higher energy density than Hydrogen.

CONS: Not as clean, produces carbon dioxide. Has a higher operating temperature of 120°C, as opposed to 80°C for hydrogen. Requires more Platinum than a hydrogen fuel cell.

Fuel Source	Energy Density ($MJdm^{-3}$)	Specific Energy ($MJkg^{-1}$)
Compressed Hydrogen	1.9	120
Methanol	16	20

Liquified Natural Gas	21	50
Liquid Propane	27	46
Gasoline	32	46

As you can see hydrogen has a very favorable Specific Energy due to its low molar mass. One mole of H_2 would require approximately 24 Liters. That same volume could hold 545 moles of methanol. Compressing the hydrogen would add holding tanks and compression motors, making its weight advantage less desirable. With new technologies in membranes and nano-catalysts, scientists predict we may be able to achieve fuel cells with energy densities that are five times that of methanol.

Calculations for Electrochemical Cells:

Thermodynamic Efficiency: $\Delta G/\Delta H$ = thermodynamic efficiency

H_2 (g) + 1/2O_2 (g) $\rightarrow$ H_2O (l) ΔH = -286 kJ combustion enthalpy

H_2 (g) + 1/2O_2 (g) $\rightarrow$ H_2O (g) ΔH = -242 kJ fuel cell enthalpy (notice the phase of water)

The following equation, $\Delta G° = -nFE°$, predicts the $\Delta G°$ to be -229 kJ. The thermodynamic efficiency is -229/-242 = 0.95 or 95%.

For a methanol fuel cell the following values are:

CH_3OH (l) + 3/2O_2 (g) $\rightarrow$ CO_2 (g) + 2H_2O (g)

$\Delta H_{rxn} = \sum \Delta H_f°$ prod - $\sum \Delta H_f°$ react ΔH_{rxn} = -726 kJ

And -685/-726 = 0.94 = 94%

$\Delta G° = \sum \Delta G_f°$ prod - $\sum \Delta G_f°$ react $\Delta G°$ = -685 kJ

Most fuel cells do not operate at their theoretical maximum efficiency. If a fuel cell operates at 0.7 V, the thermal efficiency can be calculated:

$\Delta G° = -nFE°$ $\Delta G° = -(2 \times 96500 \times 0.7) = -135100$ J or -135.1 kJ

Thermodynamic efficiency = -135.1/242 = 0.56 = 56%

Cell Potential Under Non-Standard Conditions:

The Nernst Equation: $E = E° - RT/nF \ln Q$

Microbial Fuel Cells:

A microbial fuel cell converts chemical energy from a substrate into electricity by anaerobic oxidation.

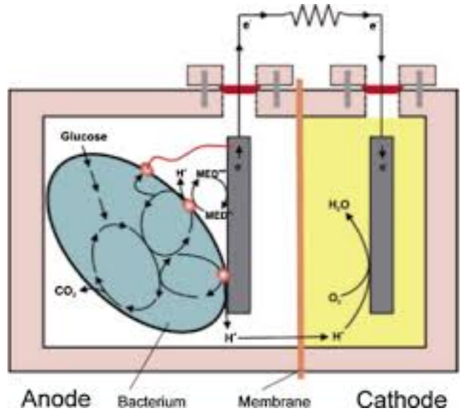
Aerobic oxidation:

$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$

Anaerobic oxidation:

$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 24H^+ + 24e'$

The bacteria live at the anode and work on substrates such as CH_3COO^-


Glucose
H⁺
MED
CO₂
H₂O
O₂
H⁺
H⁺
Anode
Bacterium
Membrane
Cathode