Electrochemistry

Atoms compete for each other's electrons

1. When chemical bonds form, electrons are either lost, gained or shared
2. Oxidation-Reduction reactions (Redox reactions)
   a. Metals
      i. lose electrons (OXIDATION)[*NOTE: as when metals combine with oxygen*]
      ii. are oxidized
      iii. are reducing agents
   b. Nonmetals
      i. gain electrons reducing their oxidation states (REDUCTION)
      ii. are reduced
      iii. are oxidizing agents
3. Example 1 - $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$

Oxidation
Is
Loss

Reduction
Is
Gain

Mg	O_2
★ loses electrons ★ gets oxidized to Mg^{2+} ★ is the reducing agent for O_2	★ gains electrons ★ gets reduced to O^{2-} ★ is the oxidizing agent for Mg

Oxidation number (Oxidation state) - number assigned to keep track of electrons based on the arbitrary assumption that shared electrons belong to the more electronegative element

1. Rules for assigning oxidation numbers
   a. Oxidation numbers for atoms that are free elements are always zero
   b. The oxidation numbers of ions are the same as the charge on the ion
   c. Some elements have only one oxidation state
      i. group 1 metals always form 1+ ions and always have a +1 oxidation state
      ii. group 2 metals always form 2+ ions and always have a +2 oxidation state
   d. Some elements usually have a particular oxidation state
      i. oxygen has a -2 oxidation state except in peroxides where it is -1 and in compounds with fluorine (OF_2) where it is +2
      ii. hydrogen has a +1 oxidation state except in hydrides with group 1 and group 2 metals
   e. the sum of the oxidation numbers
      i. in a compound it is always zero
      ii. in a polyatomic ion it is equal to the charge on the ion
2. Finding oxidation numbers
   a. apply the rules
   b. construct a table if necessary
3. When chemical bonds form, electrons are either lost, gained or shared.
   a. Metals lose electrons.
      i. When the iron, a metal, combines with oxygen, a non metal, to form rust, it loses electrons.
      ii. This causes the oxidation state to go up
      iii. This process is called oxidation even when the nonmetal is not oxygen.
   b. Nonmetals gain electrons
      i. This causes their oxidation states to go down.
      ii. This is called reduction.

Sample Problem

Find the oxidation state of the elements in $K_2Cr_2O_7$.

Element	K	Cr	O	TOTAL
Subscript	2	2	7	
Oxidation state	+1	?	-2	
Sum of oxidation states	+2	??	-14	0

[a] potassium is a group one metal; its oxidation state is always +1
[b] oxygen usually has an oxidation state of -2
[c] the sum of oxidation states of each element is the product of the subscript and the oxidation state
[d] find the –sum of the oxidation states of chromium (??) by setting the sum of all the oxidation states to zero

$$(+2) + ?? + (-14) = 0$$
$$?? = +12$$

[f] find the oxidation state of chromium (?) by dividing the sum (+12) by the subscript (2)

$$+12 \div 2 = +6$$

It is possible to tell what was oxidized and what was reduced in a chemical reaction

1. check the oxidation states of the elements before and after the reaction.
   a. The element that has an increase in oxidation state was oxidized
   b. the element that has a decrease in oxidation state was reduced.

<u>*Example*</u>

$2FeCl_2 + Cl_2 \rightarrow 2FeCl_3$

$Fe^{+2} \rightarrow Fe^{+3}$ Iron was oxidized

$Cl^0 \rightarrow Cl^{-1}$ Chlorine was reduced

2. Example 1: Magnesium burns
   a. Half reactions — reaction showing either a gain or loss of electrons
      i. $2Mg^0 \rightarrow 2Mg^{2+} + 4e^-$
      ii. $O_2^0 + 4e^- \rightarrow 2O^{2-}$
   b. Net equation (REDOX REACTION)— combination of the half reactions such that the number of electrons lost equals the number of electrons gained

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

3. Example 2 - More active metals replace less active metals in compounds by transferring electrons to them
   a. Sample Reaction:
      $Zn(s) + Cu(NO_3)_2(aq) \rightarrow Zn(NO_3)_2(aq) + Cu(s)$
   b. Half reactions — reaction showing either a gain or loss of electrons
      i. $Zn^0 \rightarrow Zn^{2+} + 2e^-$
      ii. $Cu^{2+} + 2e^- \rightarrow Cu^0$
   c. Net equation — combination of the half reactions such that the number of electrons lost equals the number of electrons gained

$$Cu^{2+} + Zn^0 \rightarrow Zn^{2+} + Cu^0$$

   d. Spectator ions — ions that are present during a reaction but do not participate in the reaction:

$$2NO_3^-$$

Balancing by the half-reaction method (ion-electron method)

<u>Balance</u>

$HNO_3 + KI \rightarrow KNO_3 + I_2 + NO + H_2O$

Step 1: Write the ionic equation

$H + NO_3 + K + I \rightarrow K + NO_3 + I_2 + NO + H_2O$

Step 2: Determine the oxidation states

$\overset{+1}{H} + \overset{+5}{N}\overset{-2}{O_3} + \overset{+1}{K} + \overset{-1}{I} \rightarrow \overset{+1}{K} + \overset{+5}{N}\overset{-2}{O_3} + \overset{0}{I_2} + \overset{+2}{N}\overset{-2}{O} + \overset{+1}{H_2}\overset{-1}{O}$

Step 3: Write oxidation half reaction, balancing atoms and charge

$2I^{-1} \rightarrow I_2^0 + 2e^-$

Step 4: Write reduction half reaction, balancing atoms and charge

$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$

Step 5: Conserve charge (electrons lost = electrons gained)

$6I^{-1} \rightarrow 3I_2^0 + 6e^-$

$2NO_3^- + 8H^+ + 6e^- \rightarrow 2NO + 4H_2O$

Step 6: Combine half reactions

$2NO_3^- + 6I^{-1} + 8H^+ \rightarrow 3I_2^0 + 2NO + 4H_2O$

Step 7: Combine ions to form compounds in original equation

$8HNO_3 + 6KI \rightarrow 6KNO_3 + 3I_2 + 2NO + 4H_2O$

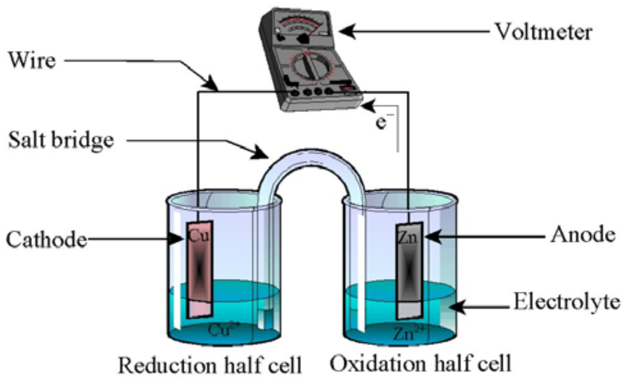
Activity Series

1. More active metals can replace less active metals
2. Metals that are more active than hydrogen can replace hydrogen
3. Hydrogen is used as a standard for comparing the activity of metals
    a. Lithium (*MOST ACTIVE*)
    b. Rubidium
    c. Potassium
    d. Cesium
    e. Barium
    f. Strontium
    g. Calcium
    h. Sodium
    i. Magnesium
    j. Aluminum
    k. Titanium
    l. Manganese
    m. Zinc
    n. Chromium
    o. Iron
    p. Nickel
    q. Tin
    r. Lead
    s. **HYDROGEN**
    t. Copper
    u. Mercury
    v. Silver
    w. Platinum
    x. Gold (*LEAST ACTIVE*)
4. Acids release hydrogen when they react with active metals
5. Active metals corrode easily
    a. Definition: CORROSION — loss of metallic properties due to action of air, water, and chemicals
    b. Examples
        i. Rust: $4Fe + 3O_2 \rightarrow 2Fe_2O_3$
        ii. Action of Acids: $2Fe + 6HCl \rightarrow 2FeCl_3 + 3H_2$
6. Spontaneous reactions - replacement of a less active metal by a more active metal occurs spontaneously

Electrochemical cells

1. Functioning of the electrochemical cell
   a. During a single replacement reaction, more active metals transfer electrons to less active metals
      i. the more active metal is oxidized
      ii. the less active metal is reduced
   b. If the oxidation and reduction half reactions are physically separated and attached by a wire, electrons will flow through the wire during the reaction
2. Parts of an electrochemical cell
   a. electrodes
      i. anode — place where oxidation occurs
      ii. cathode — place where reduction occurs
   b. half cells — separate containers in which oxidation and reduction half reactions occur

The Electrode Zoo	
AN OX	**– AN**ode = **OX**idation
RED CAT	**– CAT**hode = **RED**uction



   c. U-tube or salt bridge — lets ions travel between half cells to complete the circuit
3. Voltaic Cells (Spontaneous Reactions) — a system that uses a chemical reaction to produce electricity
   a. Examples: [1] lead acid storage battery (automobile battery); [2] dry cell (zinc container anode, carbon center post cathode)

Voltage of electrochemical cells

1. Standard electrode potentials — the international standard for E^0 uses reduction potentials
2. all half reactions are compared to hydrogen (E^0=0)
3. all half reactions can be read in reverse as oxidations in which case the sign of the voltage, E^0, is changed
4. the net voltage is the sum of the voltages of the oxidation half reactions and the reduction half reactions (see chart)

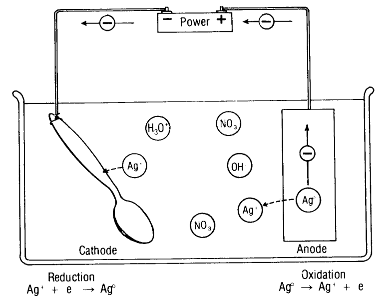
$Zn^0 \rightarrow Zn^{2+} + 2e^- \quad E^0 = 0.76v$

$\underline{Cu^{2+} + 2e^- \rightarrow Cu^0 \quad E^0 = 0.34v}$

$Cu^{2+} + Zn^0 \rightarrow Zn^{2+} + Cu^0 \quad E^0 = 1.10v$

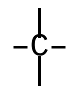
Electrolytic cells (Nonspontaneous Reactions)

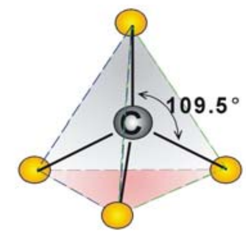
1. Definition — a system that uses electricity to cause a chemical reaction
2. Examples
   a. recharging a car battery:
   $$2PbSO_4 + 2H_2O \rightarrow PbO_2 + Pb + 2H_2SO_4$$
   b. electrolysis of molten sodium chloride
   $$2NaCl \rightarrow 2Na^0 + Cl_2^0$$
   c. electroplating

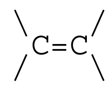


<u>Organic</u>

Nature of Carbon

1. Family - Group group 14
    a. Metalloid - can bond with metals and nonmetals
    b. Most active member of family
    c. Electron configuration
        i. 4 valence electrons
        ii. can bond with up to four elements at once
2. Bonding
    a. forms compounds by covalent bonding
        i. single bond - one shared pair of electrons 
            (1) forms a regular tetrahedron



        ii. double bond - two shared pairs of electrons 
        iii. triple bond - three shared pairs of electrons $-C\equiv C-$
    b. forms bonds with other elements or with other carbons
    c. can form chains of carbon of unlimited length
        i. chains can be straight
        ii. chains can be branched
        iii. chains can be closed to form rings
3. The variety and complexity of carbon compounds is unlimited

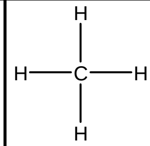
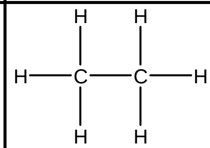
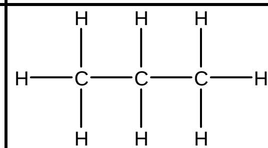
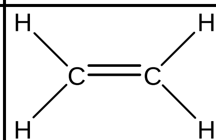
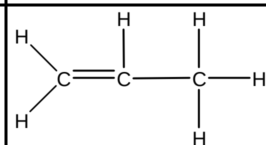
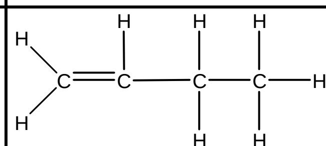
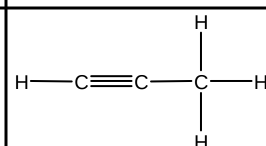
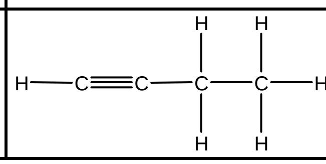
Characteristics of organic compounds

i. Formed as a result almost exclusively of covalent bonding
ii. Generally nonpolar
iii. Generally insoluble in water
    (1) usually soluble in nonpolar solvents (other organic compounds)
iv. Nonelectrolytes except organic acids which are weak electrolytes
v. Have low melting points (due to weak intermolecular forces that hold them together)

Hydrocarbons

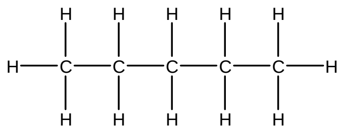
1. Definition - compounds composed of only hydrogen and carbon
2. Homologous series - group of organic compounds with similar properties and related structures (differ from each other by CH_2)
    a. Aliphatic - hydrocarbon chains
        i. Saturated
            (1) Definition - has no bonds that can be broken to add extra hydrogens
            (2) called **Alkanes**
                (a) family of hydrocarbons with all single bonds
                (b) general formula C_nH_{2n+1}
                (c) named with suffix **"ANE"**
        ii. Unsaturated - has double or triple bonds that can be broken to add more hydrogens
            (1) **Alkenes**
                (a) family of hydrocarbons with one double bond
                (b) general formula C_nH2_n
                (c) named with suffix "**ENE**"
            (2) **Alkynes**
                (a) family of hydrocarbons with one triple bond
                (b) general formula C_nH_{2n-2}
                (c) named with suffix "**YNE**"

Types of formulas

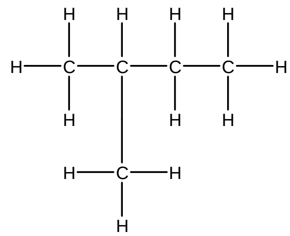
Type of Compound	Simple formula	Structural formula	Graphic formula
Alkanes	CH_4		CH_4
	C_2H_6		CH_3CH_3
	C_3H_8		$CH_3CH_2CH_3$
Alkenes	C_2H_4		CH_2CH_2
	C_3H_6		CH_2CHCH_3
	C_4H_8		$CH_2CHCH_2CH_3$
Alkynes	C_2H_2	$H-C\equiv C-H$	CHCH
	C_3H_4		$CHCCH_3$
	C_4H_6		$CHCCH_2CH_3$

3. Isomers - compounds with the same simple formula but different structures

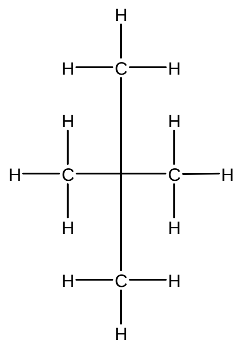
C_5H_{12}



Pentane



2-methyl butane



2,2-dimethyl propane

   a. structures must actually be different (looking different on paper is not always enough)
   b. branches of different isomers are attached on non-equivalent carbons
   c. geometric isomers *cis*, *trans*

Naming hydrocarbons

1. family: alkane, alkene, or alkyne - use suffix ANE, ENE, or YNE
2. Length of chain, length of side chain, number of side chains or functional groups, location of side chains or functional groups - use prefixes

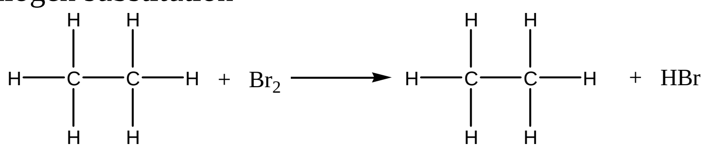
Number	Prefix			
	Carbons in Main Chain	Carbons in side chain	Number of side chains or groups	Location of side chains or groups
1	meth	methyl	-	1
2	eth	ethyl	di	2
3	prop	propyl	tri	3
4	but	butyl	tetra	4
5	pent	pentyl	penta	5
6	hex	hexyl	hexa	6
7	hept	heptyl	hepta	7
8	oct	octyl	octa	8
9	non	nonyl	nona	9
10	dec	decyl	deca	10

Table R
Organic Functional Groups

Class of Compound	Functional Group	General Formula	Example
halide (halocarbon)	$-F$ (fluoro-) $-Cl$ (chloro-) $-Br$ (bromo-) $-I$ (iodo-)	$R-X$ (X represents any halogen)	$CH_3CHClCH_3$ 2-chloropropane
alcohol	$-OH$	$R-OH$	$CH_3CH_2CH_2OH$ 1-propanol
ether	$-O-$	$R-O-R'$	$CH_3OCH_2CH_3$ methyl ethyl ether
aldehyde	$-\overset{\overset{O}{\Vert}}{C}-H$	$R-\overset{\overset{O}{\Vert}}{C}-H$	$CH_3CH_2\overset{\overset{O}{\Vert}}{C}-H$ propanal
ketone	$-\overset{\overset{O}{\Vert}}{C}-$	$R-\overset{\overset{O}{\Vert}}{C}-R'$	$CH_3\overset{\overset{O}{\Vert}}{C}CH_2CH_2CH_3$ 2-pentanone
organic acid	$-\overset{\overset{O}{\Vert}}{C}-OH$	$R-\overset{\overset{O}{\Vert}}{C}-OH$	$CH_3CH_2\overset{\overset{O}{\Vert}}{C}-OH$ propanoic acid
ester	$-\overset{\overset{O}{\Vert}}{C}-O-$	$R-\overset{\overset{O}{\Vert}}{C}-O-R'$	$CH_3CH_2\overset{\overset{O}{\Vert}}{C}OCH_3$ methyl propanoate
amine	$-\overset{\vert}{N}-$	$R-\overset{\overset{R'}{\vert}}{N}-R''$	$CH_3CH_2CH_2NH_2$ 1-propanamine
amide	$-\overset{\overset{O}{\Vert}}{C}-\overset{\vert}{N}H$	$R-\overset{\overset{O}{\Vert}}{C}-\overset{\overset{R'}{\vert}}{N}H$	$CH_3CH_2\overset{\overset{O}{\Vert}}{C}-NH_2$ propanamide

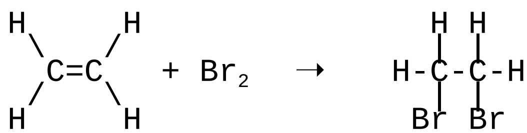
Organic Reactions

4. Combustion - burning
   a. with sufficient oxygen → CO_2 and water
      i. example: $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$
   b. with insufficient oxygen → CO and water
      i. example: $2C_3H_8 + 7O_2 \rightarrow 6CO + 8H_2O$
5. Substitution - replacement of hydrogen in saturated hydrocarbons
   a. example: halogen substitution



ethane + bromine → monobromoethane + hydrogen

6. Addition
   a. Definition = Adding two or more atoms to carbon at a point of unsaturation
   b. Characteristics
      i. take place more easily than substitutions
      ii. unsaturated bonds are more reactive than saturated bonds and alkynes are more reactive than alkenes
      iii. results in the formation of a single product
   c. Examples



      i. halogenation - occurs at room temperature
   d. Hydrogenation
      i. Definition - addition of hydrogen to an alkene or an alkyne (or other carbon compounds with double or triple bonds)
7. Fermentation - enzymatic breakdown of organic molecules during anaerobic respiration

   $C_6H_{12}O_6 \xrightarrow{zymase} 2C_2H_5OH + 2CO_2$

   glucose → ethanol + carbon dioxide
8. Esterification - formation of esters
   a. General formula: RCOOR
   b. Formation: $ROH + RCOOH \rightarrow RCOOR + H_2O$
   c. importance:
      i. fruit flavorings and aromas
      ii. lipids are formed by esterification of glycerol by fatty acids

Nuclear

Half life - the amount of time it takes for half of a radioactive sample to decay

1. Explanation
   a. During radioactive decay, high speed particles are emitted that bang into other atoms and cause them to decay
   b. As a sample decays the amount of radioactive material decreases
   c. As the size of the radioactive sample decreases, the number of particles emitted decreases
   d. As the number of particles emitted decreases, the number of collisions decreases and radioactive decay slows down
   e. Radioactive decay slows down over time in such a way that the amount of time it takes for half a sample to decay is constant regardless of the size of the sample
      i. the fraction of uranium left can be determined by comparing its mass to the mass of the lead
2. number of half lives and time elapsed
   T_e = Time elapsed $t_{½}$ = ½ life
   n = number of ½ lives f = fraction left
   $f = (½)^n$ $T_e = n(t_{½})$
3. Half Life Problems
   a. Half life problems of all types are best solved by setting up a table that shows the *number of half lives*, the *mass*, the *time elapsed*, and the *fraction left*. (any of these 4 variables can be the unknown)

Sample Problem

An ore that once contained 320 g of ^{60}Co now contains only twenty grams of the radio active material. How long has it been decaying?

Step 1: divide the mass in half repeatedly until it is reduced from 320 g to 20 g

Step 2: look up the half life and fill in the rest of the table

number of half lives	mass	time elapsed	fraction left
0	320 g	0	1 (100 %)
1	160 g	5.26 y	1/2
2	80 g	10.52 y	1/4
3	40 g	15.78 y	1/8
4	20 g	21.04 y	1/16

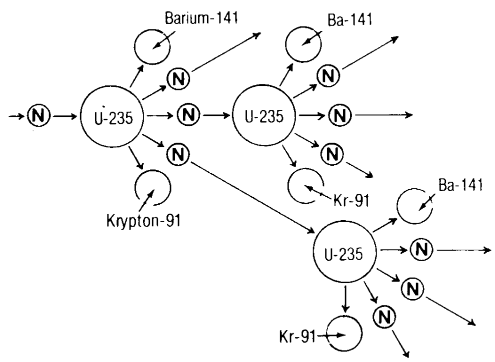
   b. Half lives of many elements are listed in *Table N*
4. Radioactive dating
   a. Carbon dating
      i. Carbon-14 is radioactive and has a half life of 5,700 years
      ii. Carbon dioxide in the air contains carbon-14
      iii. Plants take in carbon dioxide and make carbohydrates as long as they are alive
      iv. Animals eat plants as long as they are alive
      v. As soon as an organism dies, it stops taking in carbon, so its amount of c-14 begins to decrease
   b. Uranium dating
      i. Uranium-238 is radioactive and has a half life of 10^9 years
      ii. Uranium-238 is found in igneous rock
      iii. Uranium-238 decays into lead
      iv. After the rock cools, the amount of uranium-238 in the rock begins to decrease and the amount of lead begins to increase

Fission

1. Definition - a nuclear reaction in which a heavy nucleus splits into two lighter nuclei releasing neutrons and a tremendous amount of energy
   a. Cause - initiated by capture of a neutron fired at the nucleus of an atom
   b. the lighter elements that form from fission are more stable than the parent element due to greater binding energy per nucleon
2. Chain Reaction
   a. A reaction in which the neutrons released by fission of one nucleus trigger fission in other nuclei nearby
      i. Uranium-235 is unstable and splits into two smaller nuclei plus neutrons and energy.
      ii. The rate of fission can be increased by firing a neutron at the uranium atom

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

      iii. the neutrons released in the reaction can cause additional reactions



   b. Importance
      i. an uncontrolled chain reaction results in a nuclear explosion (atomic bomb)
      ii. a controlled chain reaction can be used as a source of energy (nuclear reactor)

Fusion - nuclear reaction in which the nuclei of two different isotopes of hydrogen combine

1. D-T reaction - in fusion reactors

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

   a. deuterium is obtained from heavy water extracted from water
   b. tritium is manufactured by a nuclear reaction

      $^{6}_{3}Li + ^{0}_{1}n \rightarrow ^{3}_{1}H + ^{4}_{2}He$

2. Proton-proton chain - in stars

   $^{1}_{1}H + ^{1}_{1}H \rightarrow ^{2}_{1}H + ^{0}_{+1}e$

   $^{1}_{1}H + ^{2}_{1}H \rightarrow ^{3}_{2}He$

   $^{3}_{2}He + ^{3}_{2}He \rightarrow ^{4}_{2}He + 2^{1}_{1}H$

3. Importance
   a. energy released in fusion is greater than the energy released in fission: [1] mass of new nucleus is less than the sum of the light nuclei; [2] the difference in mass is the amount of mass that was converted to energy (**$E = mc^2$**); [3] the energy provides for the greater binding energy per nucleon and the greater stability of the heavier nucleus formed
   b. principle behind the hydrogen bomb and source of energy for stars
4. High energy requirements - in order for nuclei to combine they need enough energy to overcome the forces of repulsion between like charges: [1] the magnitude of the repulsion increases with the charge; [2] only small nuclei with small charges can be used in fusion reactions ; [3] temperatures of 10^{9}°C are needed to provide the high activation energy needed for fusion

Detection and Uses of Radioactivity

1. Detection
   a. need for detection: radiation dangers
      i. ionizing radiation damages cells causing burns, rashes, or cancer
      ii. damage to reproductive cells can cause genetic defects
   b. Geiger counter
      i. structure: hollow negatively charged cylinder filled with argon gas. Has a positive wire in the center and a thin window through which radiation passes
      ii. function: radiation ionizes the argon gas. The ions are attracted to the electrodes where they create an electric pulse which is amplified to an audible click
2. Uses of radioisotopes
   a. radiotracers or radioactive labels
      i. I-131 for thyroid
      ii. $BaSO_4$ with Ba-140 to trace movement of silt in rivers
      iii. P-32 to study nutrient uptake in plants
      iv. Co-58 to trace B_{12} absorption
   b. Cancer treatment
      i. Co-60: beam of gamma rays
      ii. I-131: thyroid
   c. food preservation: Co-60