Unit 4: THERMOCHEMISTRY AND NUCLEAR CHEMISTRY

Chapter 6: Thermochemistry

6.1: The Nature of Energy and Types of Energy

Energy (***E***): - the ability to do **work** or produce **heat**.

Different Types of Energy:

1. **Radiant Energy**: - solar energy from the sun.
2. **Thermal Energy**: - energy associated with the random motion of atoms and molecules.
3. **Chemical Energy**: - sometimes refer to as **Chemical Potential Energy.** It is the energy stored in the chemical bonds, and release during chemical change.
4. **Potential Energy**: - energy of an object due to its position.

First Law of Thermodynamics: - states that energy cannot be created or destroyed. It can only be converted from one form to another. Therefore, energy in the universe is a constant.
- also known as the **Law of Conservation of Energy** ($\Sigma E_{\text{initial}} = \Sigma E_{\text{final}}$).

6.2: Energy Changes in Chemical Reactions

Heat (***q***): - the transfer of energy between two objects (internal versus surroundings) due to the difference in temperature.

Work (***w***): - when force is applied over a displacement in the same direction ($w = F \times d$).
- work performed can be equated to energy if no heat is produced ($E = w$). This is known as the **Work Energy Theorem**.

System: - a part of the entire universe as defined by the problem.

Surrounding: - the part of the universe outside the defined system.

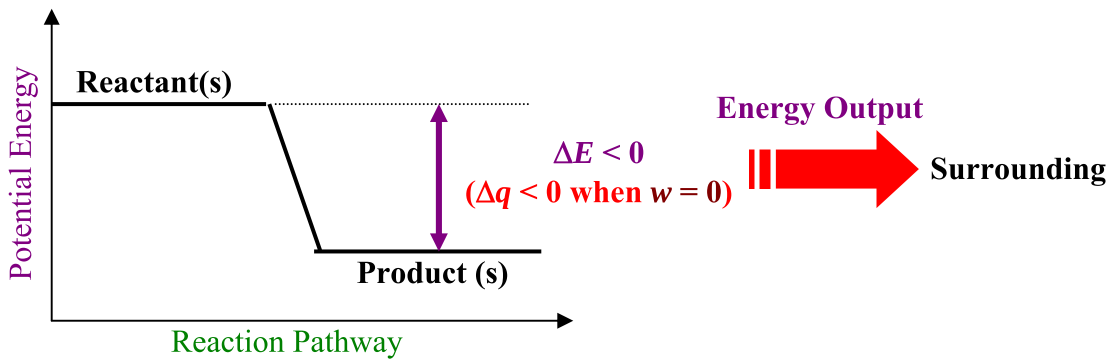
Open System: - a system where ***mass and energy*** **can interchange** freely with its surrounding.

Closed System: - a system where ***only energy*** **can interchange freely** with its surrounding but mass not allowed to enter or escaped the system.

Isolated System: - a system ***mass and energy*** **cannot interchange** freely with its surrounding.

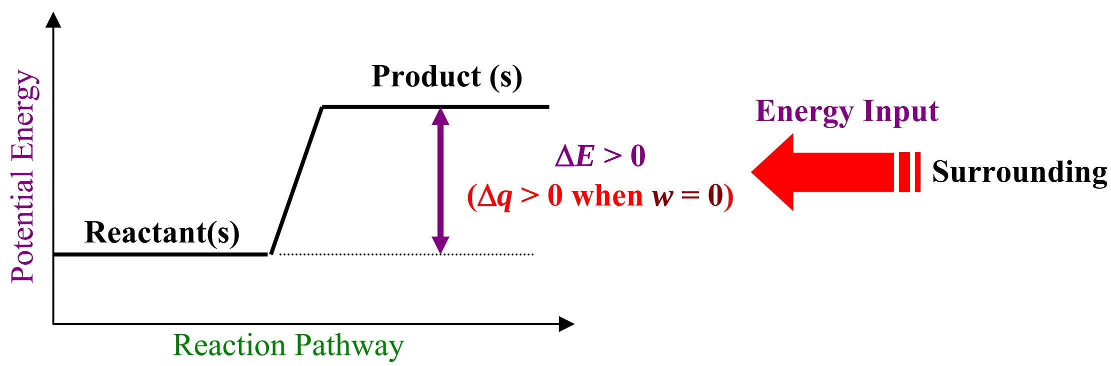
Exothermic Process (**Δ*E* < 0**): - when **energy flows "out" of the system** into the surrounding.
(Surrounding gets Warmer.)

Potential Energy Diagram for Exothermic Process



Endothermic Process (**Δ*E* > 0**): - when **energy flows into the system** from the surrounding.
(Surrounding gets Colder.)

Potential Energy Diagram for Endothermic Process



6.3: Introduction of Thermodynamics

Thermodynamics: - the study of the inter action of heat and other kinds of energy.

State of a System: - the values of all relevant macroscopic properties like composition, energy, temperature, pressure and volume.

State Function: - also refer to as **State Property** of a system at its present conditions.
- energy is a state function because of its independence of pathway, whereas work and heat are not state properties.

Pathway: - the specific conditions that dictates how energy is divided as work and heat.
- the total **energy transferred (Δ*E*)** is independent of the pathway, but the amounts of work and heat involved depends on the pathway.

Internal Energy (*E*): - total energy from work and heat within a system.

$$\Delta E = q + w$$

ΔE = Change in System's Internal Energy
q = heat ($q > 0$ endothermic; $q < 0$ exothermic)
w = work ($w > 0$ work done on the system; $w < 0$ work done by the system)

Work as Compression and Expansion

- During **expansion on the system, $w < 0$** because the system is pushing out and work is done by the system **(energy output to the surrounding)**.
- During **compression on the system, $w > 0$** because the system is being pressed by the surround and work is done on the system **(energy input by the surrounding)**.

$w = F \times \Delta d$ (Pressure = Force per unit of Area, $P = \frac{F}{A}$ or $F = PA$)

$w = (PA) \times \Delta d$ (Substitute PA as Force; $A \times \Delta d$ = Volume – 3 dimensions)

$\boldsymbol{w = -P\,\Delta V}$ (During Expansion $V\uparrow$, and $w\downarrow$. $\therefore$ Negative is added to $P\Delta V$)

$\boxed{w = -P\,\Delta V}$
(1 L • atm = 101.3 J)

Example 1: Calculate the change in internal energy of a system during an exothermic process that releases 45 kJ of energy while there was 12 kJ of work done on the system.

$q = -45$ kJ (exothermic)
$w = +12$ kJ (work done on the system)
$\Delta E = ?$

$\Delta E = q + w = (-45 \text{ kJ}) + (+12 \text{ kJ})$

$\Delta E = -33$ kJ

Example 2: A steam hydraulic system received 850 kJ from the condensation of steam into water and the volume of the piston has decreased from 12.5 L to 70.0 mL. Assuming the pressure in the piston is at 1.25 atm, determine the change in the internal energy of this hydraulic system.

$q = +850$ kJ (endothermic)
$\Delta V = 0.0700 \text{ L} - 12.5 \text{ L} = -12.43 \text{ L}$
$P = 1.25$ atm
$\Delta E = ?$

$\Delta E = q + w = q + (-P\,\Delta V)$
$\Delta E = (+850 \text{ kJ}) + (-1.25 \cancel{\text{atm}} \times -12.43 \cancel{\text{L}} \times 0.1013 \text{ kJ} / (\cancel{\text{L}} \bullet \cancel{\text{atm}}))$

$\Delta E = +852$ kJ

Assignment
6.1 to 6.3 pg. 255 #2, 3, 7 to 11, 13 to 20

6.4: Enthalpy of Chemical Reactions

Enthalpy (*H*): - the amount of internal energy at a specific pressure and volume (**$H = E + PV$**).

$\Delta E = q - P\Delta V$ ($\Delta E = \Delta H - P\Delta V$ Rearrange formula for enthalpy)

$\Delta H - P\Delta V = q - P\Delta V$ (Equate ΔE and simplify by cancelling $-P\Delta V$ on both sides)

$\Delta H = q$ (**Change in Enthalpy is Change in Heat of a system at constant pressure and little change in volume.**)

Change in Enthalpy in a Chemical Reaction

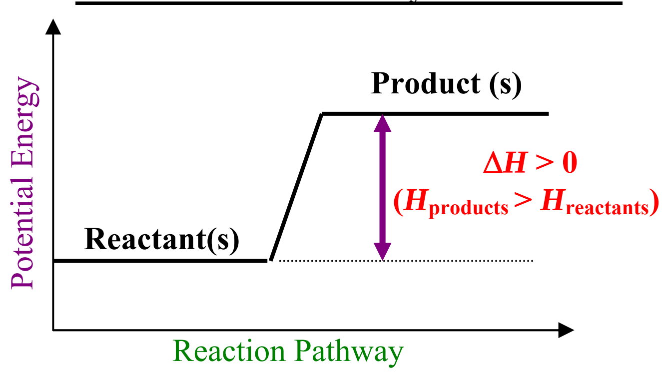
$$\Delta H = q = H_{products} - H_{reactants}$$

$\Delta H > 0$ Endothermic Reaction
$\Delta H < 0$ Exothermic Reaction

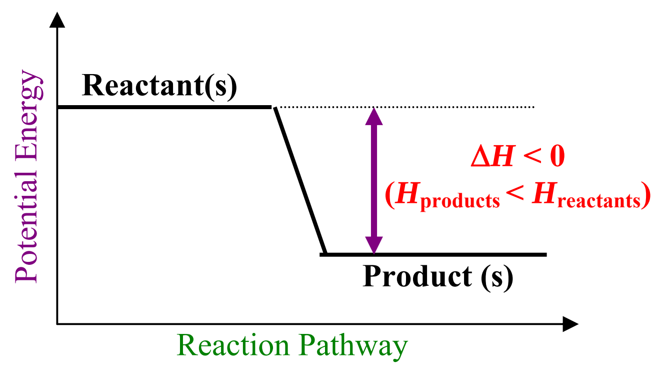
$$\Delta H = n\Delta H_{rxn}$$

ΔH = Change in Enthalpy **n = moles**
ΔH_{rxn} = Molar Enthalpy of Reaction (kJ/mol)

Potential Energy Diagram for Endothermic Chemical Reactions / Physical Processes



Potential Energy Diagram for Exothermic Chemical Reactions / Physical Processes



Writing ΔH Notations with Chemical Equations / Physical Process:

a. Endothermic Reactions / Processes

Reactant(s) + Heat $\rightarrow$ Product(s) **OR** **Reactant(s) $\rightarrow$ Product(s) $\Delta H = +$____ kJ**

Example: Water is vaporized from its liquid state.

$H_2O_{(l)} + 40.7\text{ kJ} \rightarrow H_2O_{(g)}$ or $H_2O_{(l)} \rightarrow H_2O_{(g)}$ $\Delta H = +40.7\text{ kJ}$

b. Exothermic Reactions / Processes

Reactant(s) $\rightarrow$ Product(s) + Heat **OR** **Reactant(s) $\rightarrow$ Product(s) $\Delta H = -$____ kJ**

Example: Methane undergoes combustion at constant pressure.

$CH_{4\,(g)} + 2\,O_{2\,(g)} \rightarrow CO_{2\,(g)} + 2\,H_2O_{(g)} + 802.5\text{ kJ}$ or $CH_{4\,(g)} + 2\,O_{2\,(g)} \rightarrow CO_{2\,(g)} + 2\,H_2O_{(g)}$ $\Delta H = -803\text{ kJ}$

Example 1: It takes 116.2 kJ to form 84.0 L of $NO_{2\,(g)}$ from its elements at 1.00 atm and 25.0°C. Determine the molar heat of enthalpy for the formation of $NO_{2\,(g)}$. Express the answer in proper ΔH notation.

$\Delta H = 116.2$ kJ
$V = 84.0$ L
$P = 1.00$ atm
$T = 25.0°C = 298.15$ K
$R = 0.0821\ \frac{\text{atm} \bullet \text{L}}{\text{mol} \bullet \text{K}}$

$n = ?$ $\Delta H_{rxn} = ?$

$$n = \frac{PV}{RT} = \frac{(1.00\ \cancel{\text{atm}})(84.0\ \cancel{\text{L}})}{\left(0.0821\ \frac{\cancel{\text{atm}} \bullet \cancel{\text{L}}}{\text{mol} \bullet \cancel{\text{K}}}\right)(298.15\ \cancel{\text{K}})} = 3.431636791 \text{ mol}$$

$$\Delta H = n\Delta H_{rxn} \qquad \Delta H_{rxn} = \frac{\Delta H}{n} = \frac{116.2 \text{ kJ}}{3.431636791 \text{ mol}}$$

$$\Delta H_{rxn} = 33.9 \text{ kJ/mol}$$

$N_{2\,(g)} + 2\ O_{2\,(g)} \rightarrow 2\ NO_{2\,(g)}$ **$\Delta H = 67.8$ kJ (2 mol of NO_2 in Eq)**

or $\frac{1}{2}\ N_{2\,(g)} + O_{2\,(g)} \rightarrow NO_{2\,(g)}$ **$\Delta H = 33.9$ kJ**

Example 2: Using the chemical equation from the last example, $N_{2\,(g)} + 2\ O_{2\,(g)} \rightarrow 2\ NO_{2\,(g)}$, show mathematically that the enthalpy change is approximately the same as the total internal energy change when the system is kept at a constant pressure of 1.00 atm and 25.0°C.

According to Avogadro's Law, the reaction has experienced a decrease of 1 mole of gas. ($\Delta n = -1$)

1 $N_{2\,(g)}$ + **2** $O_{2\,(g)}$ + 67.8 kJ → **2** $NO_{2\,(g)}$ **(3 moles of gaseous reactants vs. 2 moles of gaseous product)**

$\Delta E = q - P\Delta V$ (Using the Ideal Gas Law, substitute $P\Delta V = \Delta nRT$)
$\Delta E = q - \Delta nRT$ (Substitute values – using $R = 8.31$ J/(K • mol))
$\Delta E = 67.8 \text{ kJ} - (-1\ \cancel{\text{mol}})(8.31\ \cancel{\text{J}}/(\cancel{\text{K}} \bullet \cancel{\text{mol}}) \times \frac{1 \text{ kJ}}{1000\ \cancel{\text{J}}})(298.15\ \cancel{\text{K}})$

$$\Delta E = 70.3 \text{ kJ}$$

Note that the change in internal energy is 70.3 kJ. Comparing it to the enthalpy change of 68.0 kJ, the values are a close approximation (within a 5% margin). Hence, it is **acceptable to assume $\Delta H \approx \Delta E$**.

Example 3: Given that $2\ C_4H_{10\,(g)} + 13\ O_{2\,(g)} \rightarrow 8\ CO_{2\,(g)} + 10\ H_2O_{(g)} + 5317$ kJ, calculate the change in enthalpy when 28.2 g of butane is burned.

$$\Delta H_{rxn} = \frac{-5317 \text{ kJ}}{2 \text{ mol}} = -2658.5 \text{ kJ/mol}$$

(There are 2 moles of C_4H_{10} in the chemical equation for 5317 kJ.)

$$n = \frac{28.2\ \cancel{\text{g}}}{58.14\ \cancel{\text{g}}/\text{mol}}$$

$n = 0.4850361197$ mol C_4H_{10}
$\Delta H = ?$

$$\Delta H = n\Delta H_{rxn} = (0.\ 4850361197\ \cancel{\text{mol}})(-2658.5 \text{ kJ}/\cancel{\text{mol}})$$

$$\Delta H = -1.29 \times 10^3 \text{ kJ} = -1.29 \text{ MJ}$$

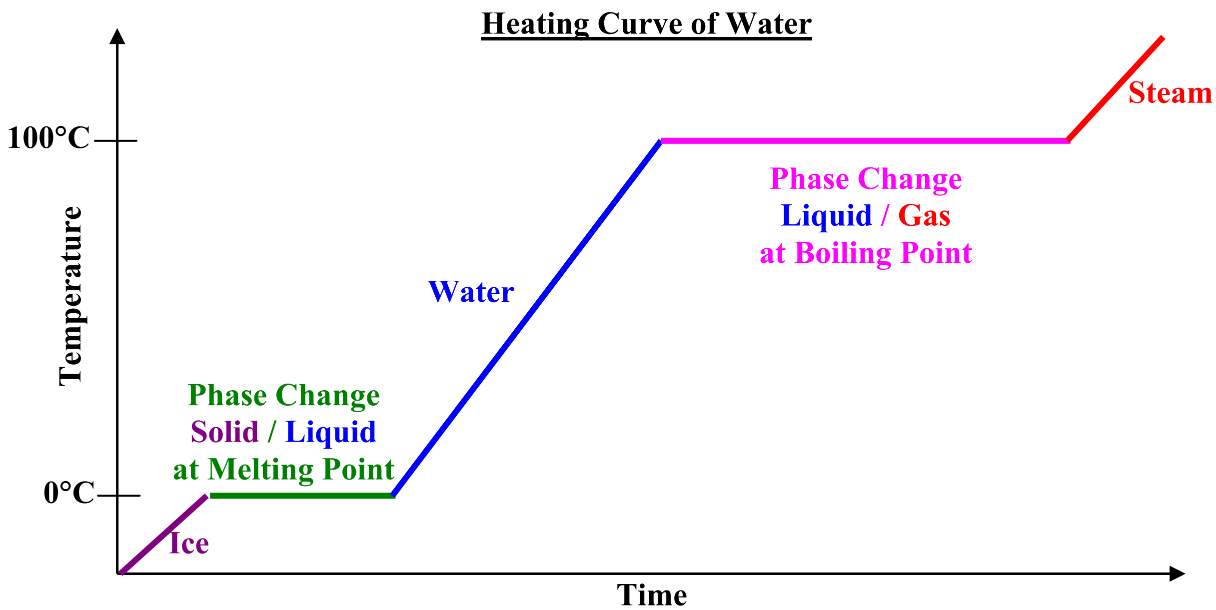
(1 MJ = 1000 kJ)

Assignment
6.4 pg. 255-256 #21, 24 to 28

6.5 & 11.8: Calorimetry and Phase Changes

Energy involved in Physical Change (Temperature or Phase Change):

Heating Curve: - a graph of temepartur versus time as a substance is heated from a solid phase to a gaseous phase.
- when a substance is undergoing a **phase change**, its **temperature remains at a constant (the plateau on the heating curve)** until all molecules aquired enough energy to overcome the intermoelcular forces nexessary. This is commonly refered to as the **potential change** of a subsatnce.
- when a substance is undergoing **temperature change** within a particular phase, it is refered to as **kinetic change** (because temeperature is also refered to as the average kinetic energy of a substance).



Molar Enthalpy of Fusion (ΔH_{fus}): - the amount of heat needed to melt one mole of substance from solid to liquid at its melting point (in kJ/mol).

Molar Enthalpy of Vaporization (ΔH_{vap}): - the amount of heat needed to evaporate one mole of substance from liquid to gas at its boiling point (in kJ/mol)

Molar Enthalpy of Sublimation (ΔH_{sub}): - the amount of heat needed to sublime one mole of substance from solid to gas (in kJ/mol).
- because sublimation involves two phase change in one step, the molar enthalpy of sublimation is the sum or the molar ethalphies of fusion and vapourization.

$$\boxed{\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}}$$

Specific Heat (*c*): - the amount of heat (J or kJ) needed to change (1 g or 1 kg) of substance by 1°C or 1 K.
- the stronger the intermolecular forces, the higher the specific heat capacity.

Heat Capacity (*C*): - the amount of heat (J or kJ) needed to a given amount of substance by 1°C or 1 K.
- usually used in a calorimeter (see section 6.5).

Physical Potential Change

$q = n\Delta H_{fus}$ $\qquad q = n\Delta H_{vap}$ $\qquad q = n\Delta H_{sub}$

q = Heat Change (J or kJ) $\qquad n$ = moles

ΔH_{fus} = Molar Enthalpy of Fusion (kJ/mol) $\qquad \Delta H_{vap}$ = Molar Enthalpy of Vaporization (kJ/mol)

ΔH_{sub} = Molar Enthalpy of Sublimation (kJ/mol) $\qquad \Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$

Physical Kinetic Change

$q = mc\Delta T$ $\qquad q = C\Delta T$

q = Heat Change (J or kJ) $\quad m$ = mass (g or kg) $\quad \Delta T$ = Change in Temperature (in °C or K)

c = Specific Heat [J/(g • °C) or kJ/(kg • °C) or J/(g • K) or kJ/(kg • K)]

C = Heat Capacity [J/°C or kJ/°C or J/K or kJ/K)]

Physical Thermodynamic Properties of Some Common Substances (at 1.00 atm and 298.15 K)

Substance	Melting Point (°C)	Boiling Point (°C)	Specific Heat Capacity [kJ/(kg • °C)]	ΔH_{fus} (kJ/mol)	ΔH_{vap} (kJ/mol)
Ice $H_2O_{(s)}$	0	----	2.03	6.01	----
Water $H_2O_{(l)}$	----	100	4.184	----	40.79
Steam $H_2O_{(g)}$	----	----	1.99	----	----
Ammonia $NH_{3\,(g)}$	−77.73	−33.34	2.06	5.66	23.33
Methanol $CH_3OH_{(l)}$	−98	64.6	2.53	3.22	35.21
Ethanol $C_2H_5OH_{(l)}$	−114.1	78.3	2.46	7.61	39.3
Aluminum $Al_{(s)}$	660	2519	0.900	10.79	294
Carbon (graphite) $C_{(s)}$	3338	4489	0.720	117	----
Copper $Cu_{(s)}$	1085	2562	0.385	12.93	300.4
Iron $Fe_{(s)}$	1538	2861	0.444	13.81	340
Mercury $Hg_{(l)}$	−39	357	0.139	23.4	59.0

Example 1: What is the change in enthalpy involved when 36.04 g of water boils from liquid to gas at 100°C?

Since this question involves phase change (vaporization) only, we need to use $q = n\Delta H_{vap}$.

ΔH_{vap} = 40.79 kJ/mol

$$n = \frac{36.04\ \cancel{g}}{18.02\ \cancel{g}/\text{mol}} = 2.000\ \text{mol}\ H_2O$$

q = ?

$q = n\Delta H_{vap}$

$q = (2.000\ \cancel{\text{mol}})(40.79\ \text{kJ}/\cancel{\text{mol}})$

q = 81.58 kJ

Example 2: How much energy is needed to heat 100.0 g of water from 20.0°C to 80.0°C?

Since this question involves temperature (kinetic) change only, we need to use $q = mc\Delta T$.

c = 4.184 J/(g • °C)
m = 100.0 g H_2O
ΔT = 80.0°C − 20.0°C = 60.0°C
q = ?

$q = mc\Delta T$
$q = (100.0\ \cancel{g})(4.184\ \text{J}/(\cancel{g} \bullet \cancel{°C}))(60.0\cancel{°C}) = 25104\ \text{J}$

$q = 2.51 \times 10^4\ \text{J} = 25.1\ \text{kJ}$

Example 3: What is the total energy needed to sublime 40.0 g of solid ammonia to gaseous ammonia? (ΔH_{fus} = 5.66 kJ/mol; ΔH_{vap} = 23.33 kJ/mol)

Since this question involves phase change (sublimation) only, we need to use $q = n\Delta H_{sub}$.

$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$
ΔH_{sub} = 5.66 kJ/mol + 23.33 kJ/mol
ΔH_{sub} = 28.99 kJ/mol

$$n = \frac{40.0\ \cancel{g}}{17.04\ \cancel{g}/\text{mol}} = 2.34741784\ \text{mol } NH_3$$

q = ?

$q = n\Delta H_{sub}$
$q = (2.34741784\ \cancel{\text{mol}})(28.99\ \text{kJ}/\cancel{\text{mol}})$

$q = 68.1\ \text{kJ}$

Example 4: What is the total energy needed to heat 18.02 g of water at 80.0°C to steam at 115°C?

For this question, we have two kinetic changes (water and steam) and one phase change (vaporization).

m = 18.02 g H_2O = 0.01802 kg H_2O

$$n = \frac{18.02\ \cancel{g}}{18.02\ \cancel{g}/\text{mol}} = 1.000\ \text{mol } H_2O$$

c_{water} = 4.184 kJ/(kg • °C)
ΔT_{water} = 100.0°C − 80.0°C = 20.0°C
ΔH_{vap} = 40.79 kJ/mol
c_{steam} = 1.99 kJ/(kg • °C)
ΔT_{steam} = 115°C − 100°C = 15°C

q_{total} = ?

$$q_{total} = \underbrace{mc_w\Delta T_w}_{\text{(water)}} + \underbrace{n\Delta H_{vap}}_{\text{(vaporization)}} + \underbrace{mc_s\Delta T_s}_{\text{(steam)}}$$

$$q_{total} = (0.01802\ \cancel{\text{kg}})(4.184\ \text{kJ}/(\cancel{\text{kg}} \bullet \cancel{°C}))(20.0\cancel{°C}) + (1.000\ \cancel{\text{mol}})(40.79\ \text{kJ}/\cancel{\text{mol}}) + (0.01802\ \cancel{\text{kg}})(1.99\ \text{kJ}/(\cancel{\text{kg}} \bullet \cancel{°C}))(15\cancel{°C})$$

q_{total} = 1.5079136 kJ + 40.79 kJ + 0.537897 kJ

$q_{total} = 42.8\ \text{kJ}$

Calorimetry: - uses the conservation of energy **(Heat Gained = Heat Lost)** to measure calories (old unit of heat: 1 cal = 4.184 J).
- physical calorimetry involves the mixing of two systems (one hotter than the other) to reach some final temperature.
- **the key to do these problems is to identify which system is gaining heat and which one is losing heat.**

Example 5: Hot water at 90.0°C is poured into 100. g of cold water at 10.0°C. The final temperature of the mixture is 70.0°C. Determine the mass of the hot water.

$m_{\text{cold water}} = 100.\text{ g}$

$c = 4.184\text{ J/(g • °C)}$

$\Delta T_{\text{hot water}} = 90.0°\text{C} - 70.0°\text{C} = 20.0°\text{C}$

$\Delta T_{\text{cold water}} = 70.0°\text{C} - 10.0°\text{C} = 60.0°\text{C}$

$m_{\text{hot water}} = ?$

Heat Lost = Heat Gained
(hot water, kinetic) (cold water, kinetic)

$$m_{hw}c\Delta T_{hw} = m_{cw}c\Delta T_{cw}$$

$$m_{hw} = \frac{m_{cw}\Delta T_{cw}}{\Delta T_{hw}} = \frac{(100.\text{ g})(60.0^\circ\text{C})}{(20.0^\circ\text{C})}$$

$$\mathbf{m_{hw} = 300.\text{ g}}$$

Example 6: A 1500. g of iron metal at 330.°C is dropped into a beaker of 1000. g of water at 25.0°C. What will be the final temperature?

$T_f = ?$

$m_{\text{Fe}} = 1500.\text{ g}$

$c_{\text{Fe}} = 0.444\text{ J/(g • °C)}$

$\Delta T_{\text{Fe}} = 330.°\text{C} - T_f$

$m_{\text{water}} = 1000.\text{ g}$

$c_{\text{water}} = 4.184\text{ J/(g • °C)}$

$\Delta T_{\text{water}} = T_f - 25.0°\text{C}$

Heat Lost = Heat Gained
(iron, kinetic) (water, kinetic)

$$m_{Fe}c_{Fe}\Delta T_{Fe} = m_w c_w \Delta T_w$$

$$(1500.\text{ g})(0.444\text{ J/(g • °C)})(330.°\text{C} - T_f) = (1000.\text{ g})(4.184\text{ J/(g • °C)})(T_f - 25.0°\text{C})$$

$$219780 - 666T_f = 4184T_f - 104600$$

$$-666T_f - 4184T_f = -104600 - 219780$$

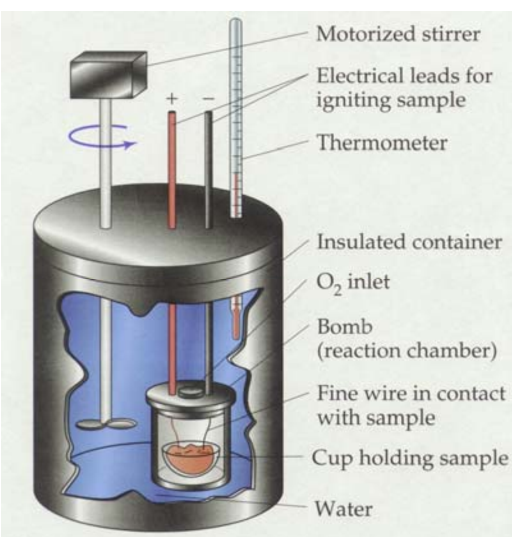
$$-4850T_f = -324380$$

$$T_f = \frac{-324380}{-4850}$$

$$\mathbf{T_f = 66.9°C}$$

Energy involved in Chemical Change (Chemical Reaction):

Molar Heat of Combustion (ΔH_{comb}): - the amount of heat released when one mole of reactant is burned with excess oxygen.
- the reaction is often exothermic and therefore $\Delta H_{comb} < 0$.



Schematic of a Bomb Calorimeter

Enthalpy of Combustion

$$\Delta H = n\Delta H_{comb}$$

ΔH = Change in Enthalpy **n = moles**
ΔH_{comb} = Molar Heat of Combustion (kJ/mol)

- we often use a *constant-volume calorimeter* (or *bomb calorimeter*) to determine ΔH_{comb} due to its well-insulated design. It is calibrated for the heat capacity of the calorimeter, C_{cal}, before being use for to calculate ΔH_{comb} of other substances. The sample is measured and burned using an electrical ignition device. Water is commonly used to absorb the heat generated by the reaction. The temperature of the water increases, allowing us to find the amount of heat generated. By applying the law of conservation of energy, we can then calculate the ΔH_{comb} of the sample.

Chemical Combustion Calorimetry

Heat Lost = Heat Gained
(Combustion Reaction) (water, kinetic)

$n_{sample}\Delta H_{comb} = C_{cal}\Delta T$ **(if bomb calorimeter is used)**

or

$n_{sample}\Delta H_{comb} = m_w c_w \Delta T$ **(if the heat absorbed by the calorimeter itself is ignored)**

Example 7: Octane, $C_8H_{18(l)}$ was burned completely to $CO_{2\,(g)}$ and $H_2O_{(l)}$ in a bomb calorimeter. The following are the observations of the experiment.

Mass of $C_8H_{18\,(l)}$ burned	32.65 g
Initial Temperature of Calorimeter and Water	16.50°C
Final Temperature of Calorimeter and Water	77.30°C
Heat Capacity of Calorimeter	24.70 kJ/°C

a. Determine the experimental molar heat of combustion of $C_8H_{18\,(l)}$.
b. The theoretical ΔH_{comb} for $C_8H_{18\,(g)}$ is −5470.1 kJ/mol, calculate the % error of this experiment.

a. $m_{octane} = 32.65\text{ g}$

$$n_{octane} = \frac{32.65\,\cancel{\text{g}}}{114.26\,\cancel{\text{g}}/\text{mol}} = 0.2857517942\text{ mol } C_8H_{18}$$

$C_{cal} = 24.70\text{ kJ/°C}$
$\Delta T = T_f - T_i = 77.30°\text{C} - 16.50°\text{C}$
$\Delta T = 60.80°\text{C}$

$\Delta H_{comb} = ?$

Heat Lost = Heat Gained
(Combustion Reaction) (water, kinetic)

$$n_{octane}\Delta H_{comb} = C_{cal}\Delta T$$

$$\Delta H_{comb} = \frac{C_{cal}\Delta T}{n_{octane}} = \frac{(24.70\text{ kJ/}\cancel{°\text{C}})(60.80\,\cancel{°\text{C}})}{(0.2857517942\text{ mol})}$$

$$\Delta H_{comb} = -5255\text{ kJ/mol}$$

(negative sign is added because ΔH_{comb} is exothermic)

b. $$\%\text{ error} = \left|\frac{\text{Theoretical} - \text{Experimental}}{\text{Theoretical}}\right| \times 100\%$$

$$\%\text{ error} = \left|\frac{(-5470.1\text{ kJ/mol}) - (-5255\text{ kJ/mol})}{(-5470.1\text{ kJ/mol})}\right| \times 100\%$$

$$\%\text{ error} = 3.932\%$$

(The small % error means the bomb calorimeter was a good heat insulator.)

Molar Heat of Reaction (ΔH_{rxn}): - the amount of heat released when one mole of reactant undergoes various chemical changes.
- examples are **ΔH_{comb}, ΔH_{neut} (neutralization), ΔH_{ion} (ionization).**

Enthalpy of Chemical Reactions

$\Delta H = n\Delta H_{rxn}$ $\Delta H = n\Delta H_{neut}$ $\Delta H = n\Delta H_{ion}$ $\Delta H = n\Delta H_{comb}$

ΔH = Change in Enthalpy **n = moles**
ΔH_{rxn} = Molar Heat of Reaction (kJ/mol) **ΔH_{neut} = Molar Heat of Neutralization (kJ/mol)**
ΔH_{ion} = Molar Heat of Ionization (kJ/mol) **ΔH_{comb} = Molar Heat of Combustion (kJ/mol)**

Constant-Pressure Calorimeter (or *Styrofoam Calorimeter*) - commonly used to determine ΔH_{neut}, ΔH_{ion}, ΔH_{fus}, ΔH_{vap}, ΔH_{rxn} of non-combustion reaction. First, the sample's mass is measured. Water is commonly used to absorb or provide the heat for the necessary change. The initial and final temperatures of the water are recorded, allowing us to find the amount of heat change. By applying the law of conservation of energy, we can then calculate the necessary molar enthalpy of change.

A Simple Styrofoam Calorimeter

Non-Combustion Calorimetry

Heat Gained /Lost = Heat Lost / Gained
(Non-Combustion Change) (water, kinetic)

$n_{sample}\Delta H_{\text{rxn}} = m_w c_w \Delta T$ **(non-combustion chemical change)**

$n_{sample}\Delta H_{\text{fus}} = m_w c_w \Delta T$ **(physical change - molar heat of fusion)**

$n_{sample}\Delta H_{\text{vap}} = m_w c_w \Delta T$ **(physical change - molar heat of vapourization)**

$m_{sample}c_{sample}\Delta T_{sample} = m_w c_w \Delta T_w$ **(physical change – specific heat)**

Example 8: When 250.0 mL of $HNO_{3\,(aq)}$ at 0.300 mol/L is reacted with 250.0 mL of $KOH_{(aq)}$ at 0.300 mol/L, the temperature of the final mixture reached 28.60°C from 22.10°C. Determine the molar heat of neutralization between $HNO_{3\,(aq)}$ and $KOH_{(aq)}$.

The reaction is acid-base neutralization and will produce water as a result.

$$HNO_{3\,(aq)} + KOH_{(aq)} \rightarrow H_2O_{(l)} + KNO_{3\,(aq)}$$

Assuming $KNO_{3\,(aq)}$ does not affect the specific heat of water, we would have **500.0 mL of water produced**. Since we have **equal moles of acid and base (0.300 mol/L × 0.2500 L = 0.0750 mol)**, the ΔH_{neut} for HNO_3 would be the same as KOH.

$n_{\text{acid}} = n_{\text{base}} = 0.0750$ mol

$m_w = 0.5000$ kg (500.0 mL is produced)
$c_w = 4.184$ kJ/(kg • °C)

$\Delta T = 28.60°\text{C} - 22.10°\text{C}$
$\Delta T = 6.50°\text{C}$

Heat Lost = Heat Gained
(Neutralization) (water, kinetic)

$$n_{acid}\Delta H_{\text{neut}} = m_w c_w \Delta T$$

$$\Delta H_{\text{neut}} = \frac{m_w c_w \Delta T}{n_{\text{acid}}}$$

$$\Delta H_{\text{neut}} = \frac{(0.5000\,\cancel{\text{kg}})(4.184\,\text{kJ}/(\cancel{\text{kg}} \bullet \cancel{°\text{C}}))(6.50\,\cancel{°\text{C}})}{(0.0750\,\text{mol})}$$

$$\Delta H_{\text{neut}} = -181\ \text{kJ/mol}$$

(negative sign is added due to increased surrounding temperature - an exothermic reaction)

Assignment

11.8 pg. 496-499 #62, 63, 67, 75, 77, 78, 80, 83, 84, 129, 135, 137, 140
6.5 pg. 256 #29 to 38

6.6: Standard Enthalpies of Formation and Reaction

Standard State: - standard conditions of 1 atm and 25°C. It is denote by a superscript "^{o}".

Standard Molar Enthalpy of Formation (ΔH^{o}_{f}): - the amount of heat required / given off to make 1 mole of compound from its elemental components under standard conditions.

- the **Molar Heat of Formation of ALL ELEMENTS is 0 kJ**.
- the **state of the compound affects the magnitude of H_f**.

($H_2O_{(g)}$ has $\Delta H^{o}_{f} = -241.8$ kJ/mol; $H_2O_{(l)}$ has $\Delta H^{o}_{f} = -285.8$ kJ/mol)

(See Appendix 3 on pg. A8 to A12 in the Chang 9th ed. Chemistry textbook for a list of ΔH°_{f})

Standard Enthalpy of Formation (Chemical)

$$\Delta H = n\Delta H^{o}_{f}$$

ΔH = Change in Enthalpy **n = moles** **ΔH^{o}_{f} = Standard Molar Enthalpy of Formation (kJ/mol)**

Example 1: Find the standard molar enthalpy of formation for table salt given that its formation reaction, $2\text{ Na}_{(s)} + \text{Cl}_{2\,(g)} \rightarrow 2\text{ NaCl}_{(s)} + 822\text{ kJ}$, at standard conditions.

$\Delta H = -822$ kJ
$n = 2$ mol of NaCl
ΔH^{o}_{f} = ?

$$\Delta H = n\Delta H^{o}_{f}$$

$$\Delta H^{o}_{f} = \frac{\Delta H}{n} = \frac{-822\text{ kJ}}{2\text{ mol}}$$

$$\Delta H^{o}_{f} = -411\text{ kJ/mol}$$

Example 2: What is the amount of heat absorbed / released when 100. g of $CO_{2\,(g)}$ is produced from its elements (CO_2 has $\Delta H^{o}_{f} = -393.5$ kJ/mol)?

$$n = \frac{100.\ \cancel{\text{g}}}{44.01\ \cancel{\text{g}}/\text{mol}} = 2.272210861\text{ mol CO}_2$$

$\Delta H^{o}_{f} = -393.5$ kJ/mol

ΔH = ?

$$\Delta H = n\Delta H^{o}_{f}$$

$$\Delta H = (2.272210861\ \cancel{\text{mol}})(-393.5\text{ kJ}/\cancel{\text{mol}})$$

$\Delta H = -894$ kJ (894 kJ is released)

Example 3: Iron (III) oxide, rust, is produced from its elements, iron and oxygen. What is the mass of rust produced when 1.20 MJ is released when iron is reacted with oxygen ($\Delta H^{o}_{f} = -822.2$ kJ/mol for Fe_2O_3)?

$\Delta H = -1.20\text{ MJ} = -1.20 \times 10^{3}$ kJ (exothermic)
$\Delta H^{o}_{f} = -822.2$ kJ/mol
$M = 159.7$ g/mol Fe_2O_3

n = ? **m = ?**

$$\Delta H = n\Delta H^{o}_{f}$$

$$n = \frac{\Delta H}{\Delta H^{\circ}_{f}} = \frac{-1.20\times10^{3}\ \cancel{\text{kJ}}}{-822.2\ \cancel{\text{kJ}}/\text{mol}} = 1.459498905\text{ mol}$$

$$m = nM = (1.459498905\ \cancel{\text{mol}})(159.7\text{ g}/\cancel{\text{mol}})$$

$m = 233$ g

Example 4: Calculate the standard molar enthalpy of formation of silver (I) oxide when 91.2 g of Ag_2O is produced from its elements and 12.2 kJ of heat is released from the process.

$$n = \frac{91.2\ \cancel{\text{g}}}{231.74\ \cancel{\text{g}}/\text{mol}} = 0.3935444895\text{ mol Ag}_2\text{O}$$

$\Delta H = -12.2$ kJ (exothermic)

ΔH^{o}_{f} = ?

$$\Delta H = n\Delta H^{o}_{f}$$

$$\Delta H^{o}_{f} = \frac{\Delta H}{n} = \frac{-12.2\text{ kJ}}{0.3935444895\text{ mol}}$$

$\Delta H^{o}_{f} = -31.0$ kJ/mol

Standard Molar Enthalpy of Reaction (ΔH^o_{rxn}): - the amount of heat involved when 1 mol of a particular product is produced or 1 mol of a particular reactant is consumed under standard conditions of 1 atm and 25°C.
- it is equal to **the difference between of all enthalpies of products and all enthalpies of reactants**.
- if the reaction is a **combustion**, it is called the **molar heat of combustion**.

(*Note*: In hydrocarbon combustion, assume all products are gaseous unless otherwise stated.)

Direct Method to determine Standard Enthalpy of Reaction

$$\Delta H^o_{rxn} = \Sigma H^o_{products} - \Sigma H^o_{reactants}$$

ΔH^o_{rxn} = Change in Enthalpy of Reaction
$\Sigma H^o_{products}$ = Sum of Heat of Products (from all $n\Delta H^o_f$ of products)
$\Sigma H^o_{reactants}$ = Sum of Heat of Reactants (from all $n\Delta H^o_f$ of reactants)

Example 5: Propane is a clean burning fossil fuel that is widely used in outdoor barbecue.
a. Calculate the standard molar enthalpy of combustion for propane.
($\Delta H^o_f\ C_3H_8 = -103.9$ kJ/mol; $\Delta H^o_f\ CO_2 = -393.5$ kJ/mol; $\Delta H^o_f\ H_2O_{(g)} = -241.8$ kJ/mol)
b. Draw its potential energy diagram.
c. How much energy will be absorbed or released when 15.0 g or propane is burned?

a. We have to first write out a balance equation for the combustion of propane.

	$C_3H_8\,_{(g)}$	+	$5\ O_2\,_{(g)}$	$\rightarrow$	$3\ CO_2\,_{(g)}$	+	$4\ H_2O_{(g)}$
ΔH^o_f:	−103.9 kJ/mol		0 kJ/mol		−393.5 kJ/mol		−241.8 kJ/mol

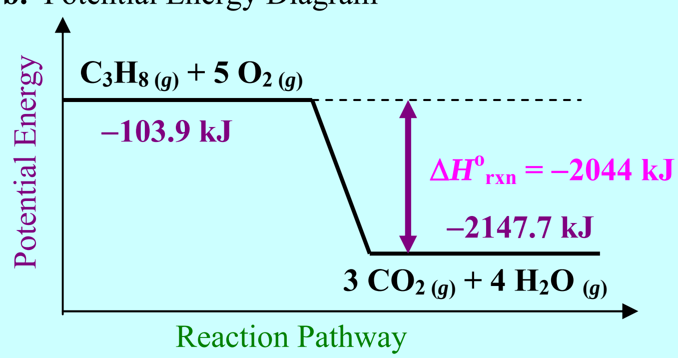
$\Delta H^o_{rxn} = \Sigma H^o_{products} - \Sigma H^o_{reactants}$

$\Delta H^o_{rxn} = [3\ \cancel{\text{mol}}\ (-393.5\ \text{kJ}/\cancel{\text{mol}}) + 4\ \cancel{\text{mol}}\ (-241.8\ \text{kJ}/\cancel{\text{mol}})] - [1\ \cancel{\text{mol}}\ (-103.9\ \text{kJ}/\cancel{\text{mol}}) + 5\ \cancel{\text{mol}}\ (0\ \text{kJ}/\cancel{\text{mol}})]$

$\Delta H^o_{rxn} = [-2147.7\ \text{kJ}] - [-103.9\ \text{kJ}] = -2043.8$ kJ

ΔH^o_{rxn} = −2044 kJ/mol of C_3H_8 burned

b. Potential Energy Diagram



c. From part a., for every 1 mol of C_3H_8 burned, 2043.8 kJ is released.

$$n = \frac{15.0\ \cancel{\text{g}}}{44.10\ \cancel{\text{g}}/\text{mol}} = 0.3401360544\ \text{mol}\ C_3H_8$$

$\Delta H^o_{rxn} = -2043.8$ kJ/mol **ΔH = ?**

$\Delta H = n\Delta H^o_{rxn}$

$\Delta H = (0.\ 3401360544\ \cancel{\text{mol}})(-2043.8\ \text{kJ}/\cancel{\text{mol}})$

ΔH = −695 kJ (695 kJ is released)

Example 6: Find the amount of heat released when 34.9 g of butane gas is burned at standard conditions. (ΔH^o_f C_4H_{10} = −124.7 kJ/mol; ΔH^o_f CO_2 = −393.5 kJ/mol; ΔH^o_f $H_2O_{(g)}$ = −241.8 kJ/mol)

We have to first write out a balance equation for the combustion of butane.

$$2\ C_4H_{10\,(g)} + 13\ O_{2\,(g)} \rightarrow 8\ CO_{2\,(g)} + 10\ H_2O_{(g)}$$

(We have to divide all coefficients by 2 because we are calculating ΔH_{rxn} per mol of butane burned.)

$$C_4H_{10\,(g)} + \frac{13}{2}\ O_{2\,(g)} \rightarrow 4\ CO_{2\,(g)} + 5\ H_2O_{(g)}$$

ΔH_f: −124.7 kJ/mol   0 kJ/mol   −393.5 kJ/mol   −241.8 kJ/mol

$\Delta H^o_{rxn} = \Sigma H^o_{products} - \Sigma H^o_{reactants}$

ΔH^o_{rxn} = [4 $\cancel{mol}$ (−393.5 kJ/$\cancel{mol}$) + 5 $\cancel{mol}$ (−241.8 kJ/$\cancel{mol}$)] − [1 $\cancel{mol}$ (−124.7 kJ/$\cancel{mol}$) + $\frac{13}{2}$ $\cancel{mol}$ (0 kJ/$\cancel{mol}$)]

ΔH^o_{rxn} = [−2783 kJ] − [−124.7 kJ]

ΔH_{rxn} = −2658.3 kJ/mol of C_4H_{10} burned

$n = \dfrac{34.9\ \cancel{g}}{58.14\ \cancel{g}/mol}$ = 0.6002751978 mol C_4H_{10}

ΔH_{rxn} = −2658.3 kJ/mol   **ΔH = ?**

$\Delta H = n\Delta H_{rxn}$

ΔH = (0.6002751978 $\cancel{mol}$)(−2658.3 kJ/$\cancel{mol}$) = −1595.7 kJ

ΔH = −1.60 MJ (1.60 MJ is released)

Example 7: When 10.02 g of liquid heptane is burned in the reaction vessel of a calorimeter, 1.50 L of water around the vessel increased its temperature from 20.0°C to 85.0°C. Ignoring the metallic material of the calorimeter,

a. determine the experimental standard molar enthalpy of combustion heptane.
b. find the theoretical standard molar enthalpy of combustion of heptane. ($\Delta H°_f$ heptane = −224.2 kJ/mol)
c. explain why the experimental $\Delta H°_{rxn}$ is different than its theoretical counterpart.

a. We use the conservation of heat to calculate experimental ΔH_{rxn}.

$n = \dfrac{10.02\ \cancel{g}}{100.23\ \cancel{g}/mol}$

n = 0.0999700688 mol C_7H_{16}

m_{water} = 1.50 kg (1 kg = 1 L of water)

ΔT = 85.0°C − 20.0°C = 65.0°C

c_{water} = 4.184 kJ / (kg • °C)

$\Delta H°_{rxn}$ = ?

$n\Delta H°_{rxn} = m_w c_w \Delta T$

$$\Delta H°_{rxn} = \frac{m_w c_w \Delta T}{n} = \frac{(1.50\ \cancel{kg})(4.184\ kJ/(\cancel{kg} \bullet \cancel{°C}))(65.0\ \cancel{°C})}{(0.0999700688\ mol)}$$

$\Delta H°_{rxn}$ = 4080.621377 kJ/mol (released)

Experimental $\Delta H°_{rxn}$ = −4.08 MJ/mol of C_7H_{16} burned

b. To find theoretical $\Delta H°_{rxn}$ for the combustion of heptane, we have to use the direct method.

$$C_7H_{16\,(l)} + 11\ O_{2\,(g)} \rightarrow 7\ CO_{2\,(g)} + 8\ H_2O_{(g)}$$

ΔH_f: −224.2 kJ/mol   0 kJ/mol   −393.5 kJ/mol   −241.8 kJ/mol

$\Delta H°_{rxn} = \Sigma H°_{products} - \Sigma H°_{reactants}$

$\Delta H°_{rxn}$ = [7 $\cancel{mol}$ (−393.5 kJ/$\cancel{mol}$) + 8 $\cancel{mol}$ (−241.8 kJ/$\cancel{mol}$)] − [1 $\cancel{mol}$ (−224.8 kJ/$\cancel{mol}$)]

$\Delta H°_{rxn}$ = [−4688.9 kJ] − [−224.8 kJ] = −4464.1 kJ

Theoretical $\Delta H°_{rxn}$ = −4.46 MJ/mol of C_7H_{16} burned

c. Some of the possible reasons why experimental ΔH°_{rxn} (−4.08 MJ) is different than the theoretical ΔH°_{rxn} (−4.46 MJ)

- **Some of the heat released by the reaction is absorbed by the metal calorimeter itself. Thus, the temperature gained by the water is not an exact reflection of the energy lost by the combustion.**
- **The calorimeter is not a closed system. Heat might escape into the surrounding.**
- **Even if the system is closed, the buildup of gases from the reaction would increase pressure and volume. Hence, some of the energy produced from the reaction is used to do work by the system. Thereby, lowering the heat available to warm the water.**

Example 8: $HCOOH_{(g)}$ were completely burned to $CO_{2\,(g)}$ and $H_2O_{(l)}$ in a calorimeter. The following are the observation of the experiment.

Mass of $HCOOH_{(g)}$ burned	9.22 g
Initial Temperature of Calorimeter and Water	21.5°C
Final Temperature of Calorimeter and Water	37.3°C
Heat Capacity of Calorimeter and Water	3.20 kJ/°C

a. Determine the experimental molar enthalpy of formation of $HCOOH_{(l)}$ assuming standard conditions. ($\Delta H^\circ_f\ CO_2$ = −393.5 kJ/mol; $\Delta H^\circ_f\ H_2O_{(l)}$ = −285.8 kJ/mol)

b. If the theoretical ΔH°_f for $HCOOH_{(g)}$ is −363 kJ/mol, calculate the % error of this experiment.

a. We use the conservation of heat to calculate experimental ΔH_{rxn}.

$$n = \frac{9.22\ \cancel{g}}{46.03\ \cancel{g}/\text{mol}}$$

n = 0.2003041495 mol HCOOH

C_{cal} = 3.20 kJ/°C

ΔT = 37.3°C − 21.5°C = 15.8°C

ΔH°_{rxn} = ?

$$n\Delta H^\circ_{rxn} = C_{cal}\Delta T$$

$$\Delta H^\circ_{rxn} = \frac{C_{cal}\Delta T}{n} = \frac{(3.20\ \text{kJ}/\cancel{^\circ C})(15.8\ \cancel{^\circ C})}{(0.2003041495\ \text{mol})}$$

ΔH°_{rxn} = 252.4161388 kJ/mol (released)

Experimental ΔH°_{rxn} = −252 kJ/mol of HCOOH burned

Next, we use the direct method to find the ΔH°_f of HCOOH.

$$HCOOH_{(l)} + \tfrac{1}{2}O_{2\,(g)} \rightarrow CO_{2\,(g)} + H_2O_{(l)}$$

ΔH°_f: **? kJ/mol** 0 kJ/mol −393.5 kJ/mol −285.8 kJ/mol

$$\Delta H^\circ_{rxn} = \Sigma H^\circ_{products} - \Sigma H^\circ_{reactants}$$

$$-252.4161388\ \text{kJ} = [1\ \cancel{\text{mol}}\ (-393.5\ \text{kJ}/\cancel{\text{mol}}) + 1\ \cancel{\text{mol}}\ (-285.8\ \text{kJ}/\cancel{\text{mol}})] - [1\ \text{mol}\ (\Delta H^\circ_f)]$$

$$-252.4161388\ \text{kJ} = [-679.3\ \text{kJ}] - [1\ \text{mol}\ (\Delta H^\circ_f)]$$

$$\Delta H^\circ_f = -679.3\ \text{kJ} + 252.4161388\ \text{kJ} = -426.8838612\ \text{kJ}$$

Experimental ΔH°_f of HCOOH = −427 kJ/mol

b. $$\%\ \text{error} = \left|\frac{\text{Theoretical} - \text{Experimental}}{\text{Theroretical}}\right| \times 100\%$$

$$\%\ \text{error} = \left|\frac{(-363\ \text{kJ}) - (-427\ \text{kJ})}{(-363\ \text{kJ})}\right| \times 100\%$$

% error = 17.6%

Hess's Law: - the indirect method of obtaining overall ΔH°_{rxn} of a net reaction by the **addition of ΔH°_{rxn}** of a series of reactions.

- when adding reactions, **compare the reactants and products of the overall net reaction with the intermediate (step) reactions given**. **Decide on the intermediate reactions that need to be reversed and / or multiply by a coefficient, such that when added, the intermediate products will cancel out perfectly yielding the overall net reaction**.
- if a particular **reaction** needs to be **reversed (flipped)**, the **sign of the ΔH** for that reaction will also **need to be reversed**.
- if a **coefficient** is used to **multiply** a particular **reaction**, the **ΔH** for that reaction will also **have to multiply** by that same **coefficient**.

(Check out Hess's Law Animation at http://intro.chem.okstate.edu/1314F00/Lecture/Chapter6/Hesslaw2.html)

Example 9: Calculate ΔH°_{rxn} for the reaction $N_{2\,(g)} + 2\ O_{2\,(g)} \rightarrow 2\ NO_{2\,(g)}$, when the following reactions are given.

$$N_{2\,(g)} + O_{2\,(g)} \rightarrow 2\ NO_{(g)} \qquad \Delta H^\circ_{rxn} = 180\text{ kJ}$$
$$2\ NO_{2\,(g)} \rightarrow 2\ NO_{(g)} + O_{2\,(g)} \qquad \Delta H^\circ_{rxn} = 112\text{ kJ}$$

Note that 2 NO_2 in the net reaction is on the product side, whereas 2 NO_2 in the second reaction is on the reactant side. Hence, we need to reverse the second reaction and its sign of the ΔH°_{rxn}.

$$N_{2\,(g)} + O_{2\,(g)} \rightarrow \cancel{2\ NO_{(g)}} \qquad \Delta H^\circ_{rxn} = 180\text{ kJ}$$
(Flipped) $$\cancel{2\ NO_{(g)}} + O_{2\,(g)} \rightarrow 2\ NO_{2\,(g)} \qquad \Delta H^\circ_{rxn} = -112\text{ kJ}$$
$$\mathbf{N_{2\,(g)} + 2\ O_{2\,(g)} \rightarrow 2\ NO_{2\,(g)}} \qquad \mathbf{\Delta H^\circ_{rxn} = +\ 68\text{ kJ}}$$

Example 10: Determine the ΔH°_{rxn} for the reaction $S_{(s)} + O_{2\,(g)} \rightarrow SO_{2\,(g)}$, when the following reactions are given.

$$S_{(s)} + \frac{3}{2} O_{2\,(g)} \rightarrow SO_{3\,(g)} \qquad \Delta H^\circ_{rxn} = -395.2\text{ kJ}$$
$$2\ SO_{2\,(g)} + O_{2\,(g)} \rightarrow 2\ SO_{3\,(g)} \qquad \Delta H^\circ_{rxn} = -198.2\text{ kJ}$$

a. SO_2 in the net reaction is on the product side, whereas 2 SO_2 in the second reaction is on the reactant side. Hence, we need to reverse the second reaction and its sign of the ΔH°_{rxn}.
b. There is only 1 SO_2 in the net reaction, whereas there are 2 SO_2 in the second reaction. Therefore the second reaction and its ΔH°_{rxn} need to be multiply by the coefficient of ½.

$$S_{(s)} + \frac{3}{2} O_{2\,(g)} \rightarrow SO_{3\,(g)} \qquad \Delta H^\circ_{rxn} = -395.2\text{ kJ}$$
(Flipped and × ½) $$\tfrac{1}{2}(2\ SO_{3\,(g)} \rightarrow 2\ SO_{2\,(g)} + O_{2\,(g)}) \qquad \Delta H^\circ_{rxn} = \tfrac{1}{2}(+198.2\text{ kJ})$$

$$S_{(s)} + \frac{3}{2} O_{2\,(g)} \rightarrow \cancel{SO_{3\,(g)}} \qquad \Delta H^\circ_{rxn} = -395.2\text{ kJ}$$
$$\cancel{SO_{3\,(g)}} \rightarrow SO_{2\,(g)} + \tfrac{1}{2} O_{2\,(g)} \qquad \Delta H^\circ_{rxn} = 99.1\text{ kJ}$$
$$\mathbf{S_{(s)} + O_{2\,(g)} \rightarrow SO_{2\,(g)}} \qquad \mathbf{\Delta H^\circ_{rxn} = -296.1\text{ kJ}}$$

Example 3: Find the ΔH°_{rxn} for the overall reaction of $2\ N_{2\,(g)} + 5\ O_{2\,(g)} \rightarrow 2\ N_2O_{5\,(g)}$, when the following reactions are given.

$$H_{2\,(g)} + \tfrac{1}{2}\ O_{2\,(g)} \rightarrow H_2O_{(l)} \qquad \Delta H^\circ_{rxn} = -285.8\text{ kJ}$$

$$N_2O_{5\,(g)} + H_2O_{(l)} \rightarrow 2\ HNO_{3\,(l)} \qquad \Delta H^\circ_{rxn} = -\ 76.6\text{ kJ}$$

$$\tfrac{1}{2}\ N_{2\,(g)} + \frac{3}{2}\ O_{2\,(g)} + \tfrac{1}{2}\ H_{2\,(g)} \rightarrow HNO_{3\,(l)} \qquad \Delta H^\circ_{rxn} = -174.1\text{ kJ}$$

a. $2\ N_2O_5$ in the net reaction is on the product side, whereas N_2O_5 in the second reaction is on the reactant side. Hence, we need to reverse the second reaction and its sign of the ΔH°_{rxn}.
b. There are $2\ N_2O_5$ in the net reaction, whereas there is only $1\ N_2O_5$ in the second reaction. Therefore the second reaction and its ΔH°_{rxn} need to be multiply by the coefficient of 2.
c. There are $2\ N_2$ in the next reaction on the reactant side. Since $\tfrac{1}{2}\ N_2$ is on the reactant side of the third reaction, we need to multiply the third reaction and its ΔH°_{rxn} by the coefficient of 4.
d. In order for H_2O to cancel from the first and second reactions, we have to multiple the first reaction by 2 and flipped. This is because H_2O in the second reaction has also flipped and has been multiplied by 2.

(Flipped and × 2) $\quad 2\ (H_2O_{(l)} \rightarrow H_{2\,(g)} + \tfrac{1}{2}\ O_{2\,(g)})$ $\quad \Delta H^\circ_{rxn} = 2(+285.8\text{ kJ})$

(Flipped and × 2) $\quad 2\ (2\ HNO_{3\,(l)} \rightarrow N_2O_{5\,(g)} + H_2O_{(l)})$ $\quad \Delta H^\circ_{rxn} = 2(+\ 76.6\text{ kJ})$

(× 4) $\quad 4\ (\tfrac{1}{2}\ N_{2\,(g)} + \frac{3}{2}\ O_{2\,(g)} + \tfrac{1}{2}\ H_{2\,(g)} \rightarrow HNO_{3\,(l)})$ $\quad \Delta H^\circ_{rxn} = 4(-174.1\text{ kJ})$

$$\cancel{2\ H_2O_{(l)}} \rightarrow \cancel{2\ H_{2\,(g)}} + O_{2\,(g)} \qquad \Delta H^\circ_{rxn} = +571.6\text{ kJ}$$

$$\cancel{4\ HNO_{3\,(l)}} \rightarrow 2\ N_2O_{5\,(g)} + \cancel{2\ H_2O_{(l)}} \qquad \Delta H^\circ_{rxn} = +153.2\text{ kJ}$$

$$\underline{2\ N_{2\,(g)} + 6\ O_{2\,(g)} + \cancel{2\ H_{2\,(g)}} \rightarrow \cancel{4\ HNO_{3\,(l)}} \qquad \Delta H^\circ_{rxn} = -696.4\text{ kJ}}$$

$$\mathbf{2\ N_{2\,(g)} + 5\ O_{2\,(g)} \rightarrow 2\ N_2O_{5\,(g)}} \qquad \mathbf{\Delta H^\circ_{rxn} = +\ 28.4\text{ kJ}}$$

Assignment

6.6 pg. 257−259 #39 to 42, 45 to 49, 51, 52, 54 to 56, 58, 60 to 64, 73, 74, 76, 77, 80, 81

6.7: Heat of Solution and Dilution

Hydration: - the interaction between the solute and solvent molecules during the act of dissolving to achieve a lower energy state (an exothermic change).

Molar Enthalpy of Hydration (**ΔH_{hydr}**): - the amount of heat given off per mole of solute during the process of hydration. (The solvent is usually water.)

Lattice Energy (**U** or **$\Delta H_{lattice}$**): - the amount of heat needed to break ionic bonds presented in 1 mole of ionic crystals. This is usually an endothermic process.

Molar Enthalpy of Solution (**ΔH_{soln}**): - the amount of heat needed to ***dissolve*** 1 mole of substance.
- it can easily be found ***using a constant-pressure calorimeter***.
- for ***molecular solutes,*** it involves overcoming the intermolecular forces of the solute and solvent. This is followed by the hydration process as the solute and solvent molecules come together.
- for ***ionic solutes***, it first involves overcoming the lattice energy. Finally, the ions and solvent molecules come together during hydration process.

Enthalpy of Solution

$\Delta H = n\Delta H_{soln}$ $\qquad$ $\Delta H_{soln} = U + \Delta H_{hydr}$ **(for ionic solutions)**

ΔH = Change in Enthalpy $\quad$ **n = moles** $\quad$ **ΔH_{soln} = Molar Enthalpy of Solution (kJ/mol)**
U = Lattice Energy (kJ/mol) $\quad$ **ΔH_{hydr} = Molar Enthalpy of Hydration (kJ/mol)**

(If $U > |\Delta H_{hydr}|$, then $\Delta H_{soln} > 0$ – endothermic)
(If $U < |\Delta H_{hydr}|$, then $\Delta H_{soln} < 0$ – exothermic)

Example 1: A cold pack consists of 40.0 g of NH_4NO_3 is dissolved in water. How much energy is absorbed or released into its surrounding if the ΔH_{soln} is 26.2 kJ/mol?

ΔH_{soln} = +26.2 kJ/mol ($\Delta H_{soln} > 0$; endothermic)
(Heat is absorbed from the surrounding)

$$n = \frac{40.0\ \cancel{g}}{80.06\ \cancel{g}/\text{mol}} = 0.499625281 \text{ mol } NH_4NO_3$$

ΔH = ?

$\Delta H = n\Delta H_{soln}$
$\Delta H = (0.499625281\ \cancel{\text{mol}})(26.2\ \text{kJ}/\cancel{\text{mol}})$

ΔH = 13.1 kJ absorbed

Example 2: 12.9 kJ of heat is released when $CaCl_2$ is dissolved in water, find the mass of $CaCl_2$ dissolved if the molar enthalpy of solution of $CaCl_2$ is –82.8 kJ/mol.

ΔH_{soln} = –82.8 kJ/mol ($\Delta H_{soln} < 0$; exothermic)
(Heat is released into the surrounding)
ΔH = –12.9 kJ
M = 110.98 g/mol $CaCl_2$

n = ? $\qquad$ m = ?

$$\Delta H = n\Delta H_{soln} \qquad n = \frac{\Delta H}{\Delta H_{soln}} = \frac{-12.9\ \cancel{\text{kJ}}}{-82.8\ \cancel{\text{kJ}}/\text{mol}}$$

n = 0.1557971014 mol

$m = nM$ = (0.1557971014 mol)(110.98 g/mol)

m = 17.3 g

Heat of Dilution: - the amount of heat associated during the dilution process of a solution,
- a solution that has a endothermic heat of solution (**$\Delta H_{soln} > 0$**) will have an endothermic heat of dilution.
- a solution that has a exothermic heat of solution (**$\Delta H_{soln} < 0$**) will have an exothermic heat of dilution.

(Examples: When $NaOH_{(s)}$ is dissolved to become $NaOH_{(aq)}$, it releases heat. During the dilution process, the solution gets even warmer. This is because more intermolecular forces form between the added water molecules and the ions present. More intermolecular forces or bonds form mean more heat is released. Similarly, when concentrated $H_2SO_{4\,(aq)}$ is diluted, more intermolecular forces are made and the process releases a lot of heat. Hence, we ***always add concentrated to water slowly with constant stirring***.)

Assignment
6.7 pg. 258 #66 to 68, 70

6.8: Present Sources of Energy and New Energy Sources

Fossil Fuel: - hydrocarbon fuels that came from fossils of decayed organisms.

1. **Natural Gas**: - fossil fuel that consists of mainly small alkanes (80% methane, 10% ethane, 4% propane, 2% butane, 4% nitrogen).
   - usually burns efficiently (complete combustion).

Complete Combustion: - where the products of combustion are carbon dioxide and water vapour only.
-characterized by a blue flame.

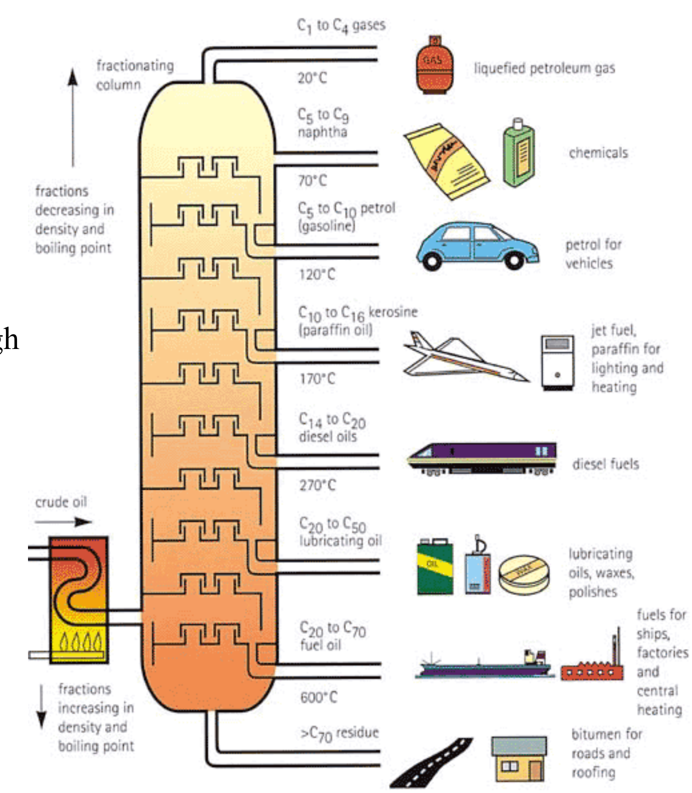
Example: Propane burns completely. $C_3H_{8\,(g)} + 5\ O_{2\,(g)} \rightarrow 3\ CO_{2\,(g)} + 4\ H_2O_{(g)}$

Incomplete Combustion: - where the main product of combustion is carbon monoxide, along with carbon dioxide and water vapour.
- happens when carbon particles started to form during combustion and deposited as soot as they cooled, or when there is insufficient oxygen.
- characterized by a yellow flame.

Example: Incomplete combustion of Propane. $C_3H_{8\,(g)} + 4\ O_{2\,(g)} \rightarrow 2\ CO_{(g)} + CO_{2\,(g)} + 4\ H_2O_{(g)}$

2. **Petroleum (Crude Oil)**: - fossil fuels that consist mainly of heavier alkanes along with small amounts of aromatic hydrocarbons, and organic compounds that contain sulfur, oxygen and nitrogen.
   - gasoline is composed of 40% of crude oil, whereas natural gas is composed of only 10%.

Fractional Distillation: - a method of heating crude oil in a tall column to separate its different components by their different boiling points.
- lighter alkanes in the natural gas will rise up to the top of the column because of their low boiling points.
- the heavier, fuel and lubricating oils will boil off at the bottom of the column due to their high boiling points.



Petroleum Refining: - a process to isolate different types of fuel from crude oil using fractional distillation or cracking.

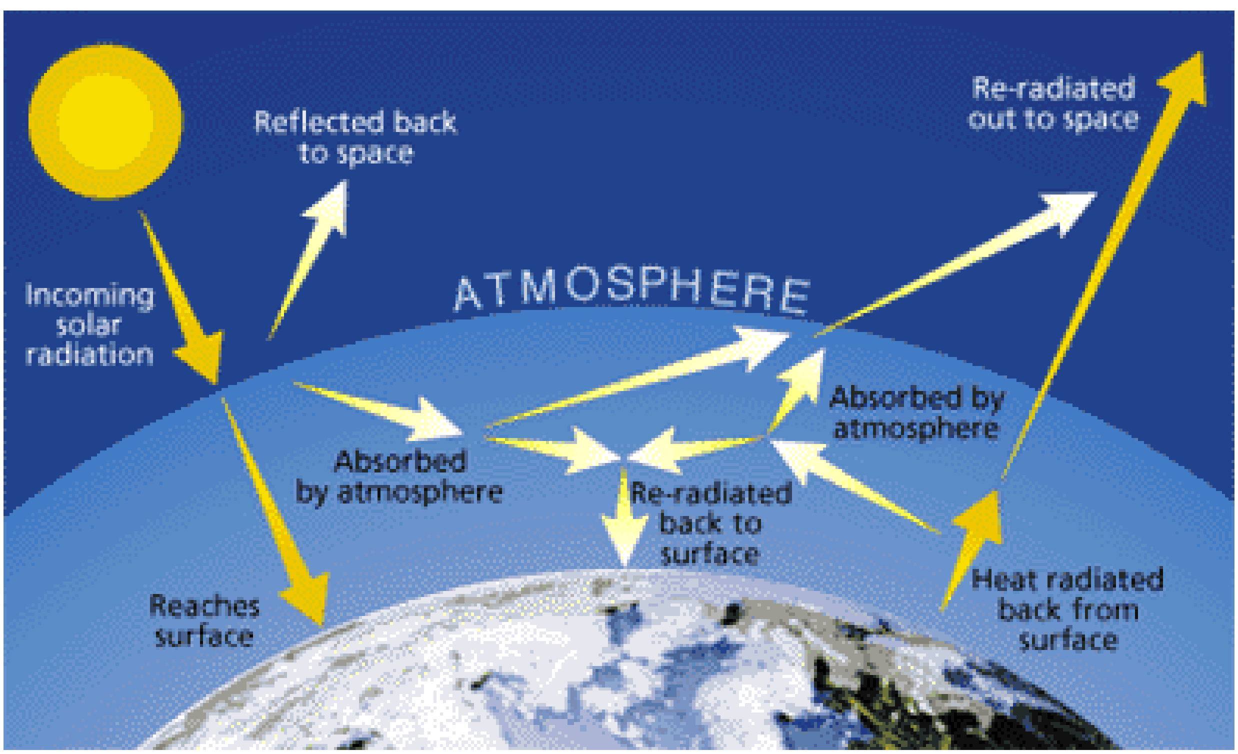
Cracking: - a chemical process whereby bigger alkanes are broken up into smaller ones using a catalyst and heat.
- since gasoline and natural gas only consists of 50% of crude oil, cracking is necessary to convert heavier fuel to more common fuel used in today's world.

Example: The Cracking of Hexadecane. $C_{16}H_{34} + 2\ H_2 \xrightarrow{\text{catalyst and heat}} C_8H_{18} + C_8H_{18}$

Reforming: - a chemical process where smaller alkanes are combined together and hydrogen is removed to form heavier alkanes or changed unbranched alkanes into branched alkanes.
- branched alkanes are easier to burn and has a higher octane value in gasoline. (isooctane or 2,2,4-trimethylpentane has the best octane rating – assigned as 100)

3. **Coal**: - a carbon-based mineral consists of very dense hydrocarbon ring compounds with high molar masses.
- leaves a lot of soot and burns incompletely.
- usually contains 7% sulfur and when combusted with oxygen gives off SO_2 and SO_3, which is the main source of air pollution and acid rain.

Greenhouse Effect: - the emission of greenhouses gases that traps more of the sun's radiant (heat) energy in the atmosphere than it occurs naturally.



Greenhouses Gases: - man-made and naturally occur gases that contribute to the Greenhouse Effect.

1. **Carbon dioxide (CO_2)** is released to the atmosphere when solid waste, fossil fuels (oil, natural gas, and coal), and wood and wood products are burned.
2. **Methane (CH_4)** is emitted during the production and transport of coal, natural gas, and oil. Methane emissions also result from the decomposition of organic wastes in municipal solid waste landfills, and the raising of livestock.
3. **Nitrous oxide** (N_2O) is emitted during agricultural and industrial activities, as well as during combustion of solid waste and fossil fuels.
4. **Hydrofluorocarbons (HFCs), Perfluorocarbons (PFCs), and Sulfur Hexafluoride (SF_6)** are very powerful greenhouse gases that are not naturally occurring that are generated in a variety of industrial processes.

   Each greenhouse gas differs in its ability to absorb heat in the atmosphere. HFCs and PFCs are the most heat-absorbent. Methane traps over 21 times more heat per molecule than carbon dioxide, and nitrous oxide absorbs 270 times more heat per molecule than carbon dioxide. Often, estimates of greenhouse gas emissions are presented in units of millions of metric tons of carbon equivalents (MMTCE), which weights each gas by its GWP value, or Global Warming Potential. (Information from US. EPA)

- Automobiles and Major Transportations account for 34% of CO_2 emissions globally (Power Plants contributes 33%; Major Industries and Home Heating contribute the remaining 33%).
- Presently 89% of Energy Productions involve the burning of Fossil Fuels (Coal, Petroleum, Natural Gas and Biomass).
- Heat and Electricity generated from combustion of fossil fuel is at most 30% efficient.

(Data from University of Michigan: http://www.umich.edu/~gs265/society/greenhouse.htm)

The Environmental Effect of Using Fossil Fuel: (Greenhouse Effect)

1. **Global Warming**: - the warming of global temperature due to an increased of greenhouse gases in the atmosphere.
2. **Rise of Water Level**: - low-lying islands and coastal area are endangered as polar icecaps melt due to the rise of temperature as a result of the greenhouse effect.
3. **Unpredicted and Erratic Climate**: - greenhouse effect is related to droughts and dry whether in many parts of the world.
4. **Deforestation**: - another cause of an increased in CO_2 level in the atmosphere. As forests disappeared, there is a lack of plants to absorb carbon dioxide using photosynthesis.
   - also causes mud and landslides, demineralization of the soil, lost animal habitats and extinction, destruction of entire ecosystems. Plants that may have important medicinal values can also be destroyed.

Alternate Energy Sources without the Emission of Greenhouse Gas

1. **Solar Energy**: - the most efficient energy source where energy from the sun is converted directly to electricity through the use of photovoltaic cells (solar panels) or heat using high efficient insulated glass and an effective water heating system.
   - technology exists but fairly expensive; requires many solar panels to generate adequate amount of electricity.

2. **Wind Power**: - the use of wind turbines to generate electricity.
   - very efficient and extremely economical, but location specific and not very reliable when there is no wind.
   - can disrupt migratory routes of birds (they get caught in the turbine), aesthetic problems for the various landscapes.

3. **Geothermal Power**: - the use of underground steam to generate electricity.
   - very efficient and reliable, but location specific.
   - geothermal power is widely use in Iceland where it is sitting on the Atlantic ridge and there are lots of hot springs.

4. **Tidal Power**: - the use of tidal current to generate electricity.
   - very efficient and somewhat reliable, but location specific.
   - tidal power involves placing electric turbines at a narrow mouth of a channel where normal tides can cause bigger current and quick rise in water levels. It is being used in the Bay of Fundy at Nova Scotia, Canada and Kvalsund at the Arctic tip of Norway.
   - tidal power can sometimes disrupt migratory routes of marine species.

5. **Hydroelectricity**: - the use of dam and reservoir to turn electric turbines as water falls from a higher level to the spillway (potential energy converted to kinetic energy to electricity).
   - very efficient and no emission of greenhouse gas.
   - location specific and very expensive to built. The reservoir flooding can destroy ecological habitats and force migrations of people from towns and villages (Aswan Dam in Egypt and the Three Gorges Dam in China displaced thousands of people and submerged ancient cities). The presence of the dam can disrupt aquatic migratory routes as well.
   - dams have a limited life span (the collection of silt and mud at the bottom of the dam has to be clear periodically to maintain the structural integrity of the dam). Dams can burst during earthquakes or poor maintenance. Flash flooding of towns along spillway is always a danger.

6. **Hydrogen Fuel**: - burning hydrogen to form water and generate heat and electricity.
   - very efficient and zero pollution.
   - hydrogen is very explosive and technologies are still needed for supplying and storing hydrogen safely in automobiles and homes.

Chapter 18: Entropy and Free Energy

18.2 & 18.3: Spontaneous Process & Entropy

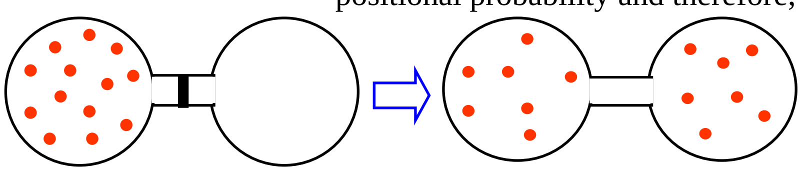
Spontaneous Process: - a thermodynamic process that happens without any external interventions.
- it does NOT indicate the speed (kinetics) of the process.

Entropy (S): - a measure of the amount of disorder or randomness.
- it mainly explains the number of molecular arrangement and the probabilities of molecular in any given arrangements.
- **unlike enthalpy, $S_{elements} \neq 0$. All $S > 0$, however, ΔS can be positive or negative.**
- **the more positive the entropy becomes, the more spontaneous is the process.**
- **most but NOT all exothermic reactions are spontaneous. Temperature of the surrounding is also an important factor.**

$$\Delta S = S_{final} - S_{inital} \text{ or } \Sigma S_{products} - \Sigma S_{reactants}$$

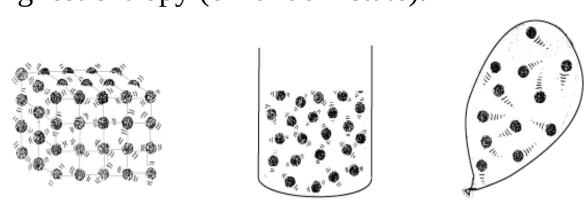
When $\Delta S > 0$, the process is Thermodynamically Spontaneous
When $\Delta S < 0$, the process is Thermodynamically Non-Spontaneous

Positional Probability: - sometimes refer to as **microstate.** It is the probability of how the molecules are arranged in a given system.
- the higher the positional probability for a set of arrangements, the higher the entropy it is for that set of arrangements.
- the complete mixing of molecules to fill a given system produces the highest positional probability and therefore, the highest entropy (or random state).



Open valve: gas spontaneously expands

More probable state (Entropy increases)



$S_{solid} < S_{liquid} << S_{gas}$

Example 1: For the following process, determine whether it is spontaneous and predict the sign of ΔS.
a. the heat from the heat vent eventually warms up the room.
b. diluting a salt solution.
c. photosynthesis occurs naturally in plants

a. the heat from the heat vent eventually warms up the room.
(Spontaneous, $\Delta S > 0$, temperature naturally goes from high to low to achieve thermodynamic equilibrium)

b. diluting a salt solution.
(Spontaneous, $\Delta S > 0$, diluted solution has more randomness and higher positional entropy than a concentrated state – volume has increased)

c. photosynthesis occurs naturally in plants.
(Non-Spontaneous, $\Delta S < 0$, even though photosynthesis occurred naturally, it does need an external intervention, namely sunlight energy to initiate the process - endothermic)

Assignment
18.2 & 18.3 pg. 810 #1 to 6

18.4: The Second Law of Thermodynamics

Second Law of Thermodynamics: - states that all spontaneous processes involve an increase in entropy in the universe. Hence, the entropy in the universe is always increasing.
- **when evaluating Spontaneity, we must evaluate the sign of ΔS of the UNIVERSE**, and not just ΔS_{sys} or ΔS_{surr}.

Second Law of Thermodynamics

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

When $\Delta S_{univ} > 0$, the process is Thermodynamically Spontaneous
When $\Delta S_{univ} = 0$, the System is at Equilibrium ($\Delta S_{sys} = -\Delta S_{surr}$)
When $\Delta S_{univ} < 0$, the process is Thermodynamically Non-Spontaneous

Example 1: The process of cleaning up a messy room of a teenager is a non-spontaneous process. However face with the threat of being grounded, most teenagers will clean up their room in a hurry. Rationalize this phenomenon using the second law of thermodynamics.

If we define the cleaning of the room as a system, then $\Delta S_{sys} < 0$. Similarly, the threat of being grounded by an outside source can be defined as the surrounding. In this case, the result of being grounded has a much lower entropy than the amount of entropy cleaning the room (they might be asked to clean the entire house and yard work). Or putting it in another way, the act of going out can be represented by $\Delta S_{surr} >> 0$ (teenagers can behave more randomly outside parental supervisions than being messy in their rooms). Since $\Delta S_{surr} >> |\Delta S_{sys}|$, most teenagers will clean their rooms due to the overall $\Delta S_{univ} > 0$.

The Effect of Temperature on Spontaneity

Entropy of the Surrounding (**ΔS_{surr}**): depends on the ΔS_{sys}, ΔH and the temperature of the surrounding.

$$\Delta S_{surr} = -\frac{\Delta H}{T}$$

ΔS_{surr} = Entropy of the Surrounding (kJ/K)
ΔH = Change in Enthalpy of the Process (kJ) **T = Temperature (K)**

When $\Delta H < 0$, $\Delta S_{surr} > 0$ **When $\Delta H > 0$, $\Delta S_{surr} < 0$**
When T is Large, $|\Delta S_{surr}|$ is Small **When T is small, $|\Delta S_{surr}|$ is Large**

1. **System is Exothermic** ($\Delta H < 0$): - **$\Delta S_{surr} > 0$ (Surrounding's Randomness Increases – Less Order)**

   a. And if ***T* is Large**, the amount of energy flows into the surrounding **cannot increase the randomness of the surrounding effectively**. Therefore, **$\Delta S_{surr} > 0$ but Small**.

   b. And if ***T* is Small**, the amount of energy flows into the surrounding **increases the randomness of the surrounding significantly**. Therefore, **$\Delta S_{surr} > 0$ and Large**.

Exothermic System		Surrounding at 1000 K
$\Delta H = -200$ kJ	⇨	$\Delta S_{surr} = -\dfrac{-200\text{ kJ}}{1000\text{ K}}$ $\Delta S_{surr} = 0.2$ kJ/K

Exothermic System		Surrounding at 10 K
$\Delta H = -200$ kJ	⇨	$\Delta S_{surr} = -\dfrac{-200\text{ kJ}}{10\text{ K}}$ $\Delta S_{surr} = 20$ kJ/K

2. **System is Endothermic** ($\Delta H > 0$): - **$\Delta S_{surr} < 0$ (Surrounding's Randomness Decreases – More Order)**

   a. And if ***T* is Large**, the amount of energy flows from the surrounding **cannot decrease the randomness of the surrounding effectively**. Therefore, **$\Delta S_{surr} < 0$ but Small**.

   b. And if ***T* is Small**, the amount of energy flows from the surrounding **decreases the randomness of the surrounding significantly**. Therefore, **$\Delta S_{surr} < 0$ and Large**.

Endothermic System		Surrounding at 1000 K
$\Delta H = 200$ kJ	⇦	$\Delta S_{surr} = -\dfrac{200\text{ kJ}}{1000\text{ K}}$ $\Delta S_{surr} = -0.2$ kJ/K

Endothermic System		Surrounding at 10 K
$\Delta H = 200$ kJ	⇦	$\Delta S_{surr} = -\dfrac{200\text{ kJ}}{10\text{ K}}$ $\Delta S_{surr} = -20$ kJ/K

***Note*: The magnitude and the sign of ΔS_{surr} alone CANNOT predict spontaneity. Spontaneity depends on ΔS_{univ} and the magnitude and the sign of ΔS_{sys} must also be taken into consideration.**

Example 2: The molar heat of fusion for water is 6.01 kJ/mol. Determine the ΔS_{surr} for the following phase change of $H_2O_{(s)} \rightarrow H_2O_{(l)}$ at –20.0°C and at 10.0°C under 1 atm.

ΔH = 6.01 kJ/mol
T_1 = –20.0°C = 253.15 K
T_2 = 10.0°C = 283.15 K

ΔS_{surr} = ?

$H_2O_{(s)} \rightarrow H_2O_{(l)}$ $\Delta H = 6.01$ kJ

$$\Delta S_{surr} = -\frac{\Delta H}{T_1} = -\frac{6.01\text{ kJ}}{253.15\text{ K}} \qquad \Delta S_{surr} = -\frac{\Delta H}{T_2} = -\frac{6.01\text{ kJ}}{283.15\text{ K}}$$

$\Delta S_{surr} = -2.37 \times 10^{-2}$ kJ/K at –20.0°C **$\Delta S_{surr} = -2.12 \times 10^{-2}$ kJ/K at 10.0°C**
$\Delta S_{surr} = -23.7$ J/K at –20.0°C **$\Delta S_{surr} = -21.2$ J/K at 10.0°C**

As predicted, $\Delta S_{surr} < 0$ due to $\Delta H > 0$ (Endothermic), and the magnitude of ΔS_{surr} is Higher at low Temperature

Example 3: The equation of $C_{(s)} + O_{2\,(g)} \rightarrow CO_{2\,(g)}$ + 393.5 kJ describes the combustion of carbon. What is the ΔS_{surr} when the reaction happens at a barbecue at –40.0°C in Anchorage, Alaska on a cold winter day compared to 40°C on a hot summer day at Phoenix, Arizona?

ΔH = –393.5 kJ/mol
T_1 = –40.0°C = 233.15 K
T_2 = 40.0°C = 313.15 K

ΔS_{surr} = ?

$C_{(s)} + O_{2\,(g)} \rightarrow CO_{2\,(g)}$ **ΔH = –393.5 kJ**

$$\Delta S_{surr} = -\frac{\Delta H}{T_1} = -\frac{-393.5\text{ kJ}}{233.15\text{ K}}$$

ΔS_{surr} = 1.69 kJ/K at –40.0°C

$$\Delta S_{surr} = -\frac{\Delta H}{T_2} = -\frac{-393.5\text{ kJ}}{313.15\text{ K}}$$

ΔS_{surr} = 1.26 kJ/K at 40.0°C

As predicted, $\Delta S_{surr} > 0$ due to $\Delta H < 0$ (Exothermic), and the magnitude of ΔS_{surr} is Higher at low Temperature.

Third Law of Thermodynamics: - states that at **0 K (absolute zero)**, the **entropy is 0** for a perfect crystal **(perfect order – no randomness)**.

General Guidelines for Entropy of System (S_{sys} or $S°$):

1. **$S°$ INCREASES when Matters change from Solid to Liquid and from Liquid to Gas.**
2. **$S°$ INCREASES with more Gaseous Molecules or Aqueous Ions (more molecules mean more possible configurations and positional probabilities).**
3. **$S°$ INCREASES with Higher Internal Temperature. Temperature is the average kinetic energy of particles. The higher the temperature, the faster they move (more Translation Motion), resulting in more randomness.**
4. **$S°$ INCREASES with the Complexity of the Molecule. The more bonds a molecule has, the more different ways it can rotate and vibrate its bonds (Rotational and Vibration Motions).**

(Check out animation at http://wine1.sb.fsu.edu/chm1046/notes/Thermody/MolBasis/MolBasis.htm)

$$\Delta S° = \Sigma S°_{products} - \Sigma S°_{reactants}$$

$\Delta S°$ = Standard Change in Entropy of a System
$\Sigma S°_{products}$ = Total Standard Entropy of all Products
$\Sigma S°_{reactants}$ = Total Standard Entropy of all Reactants

Example 4: Predict the sign of $\Delta S°$ for each reaction below. Then, calculate the $\Delta S°$ at 25.0°C and 1 atm using the given values.

a. $H_2O_{(g)} \rightarrow H_2O_{(l)}$ $S°$ ($H_2O_{(g)}$) = 189 J/(K • mol) $S°$ ($H_2O_{(l)}$) = 70 J/(K • mol)

This is a phase change from gas to liquid, $\Delta S° < 0$.
$\Delta S° = \Sigma S°_{products} - \Sigma S°_{reactants}$
$\Delta S° = (1\ \cancel{\text{mol}})(70\text{ J/(K} \bullet \cancel{\text{mol}})) - (1\ \cancel{\text{mol}})(189\text{ J/(K} \bullet \cancel{\text{mol}}))$

$\Delta S°$ = –119 J/K (per mole of steam changed to water)

b. $C_3H_{8\,(g)} + 5\ O_{2\,(g)} \rightarrow 3\ CO_{2\,(g)} + 4\ H_2O_{(g)}$

$S°\ (C_3H_{8\,(g)}) = 270$ J/(K • mol) $S°\ (O_{2\,(g)}) = 205$ J/(K • mol)
$S°\ (CO_{2\,(g)}) = 214$ J/(K • mol) $S°\ (H_2O_{(g)}) = 189$ J/(K • mol)

Since there are more moles of gaseous products, $\Delta S° > 0$.

$\Delta S° = \Sigma S°_{\text{products}} - \Sigma S°_{\text{reactants}}$

$\Delta S° = [(3\ \cancel{\text{mol}})(214\ \text{J/(K} \bullet \cancel{\text{mol}})) + (4\ \cancel{\text{mol}})(189\ \text{J/(K} \bullet \cancel{\text{mol}}))] -$
$[(1\ \cancel{\text{mol}})(270\ \text{J/(K} \bullet \cancel{\text{mol}})) + (5\ \cancel{\text{mol}})(205\ \text{J/(K} \bullet \cancel{\text{mol}}))]$

$\Delta S° = [1398\ \text{J/K}] - [1295\ \text{J/K}]$

$\Delta S° = 103$ J/K (per mole of propane burned)

c. $S_{(s)} + O_{2\,(g)} \rightarrow SO_{2\,(g)}$

$S°\ (S_{(s)}) = 33$ J/(K • mol) $S°\ (O_{2\,(g)}) = 205$ J/(K • mol) $S°\ (SO_{2\,(g)}) = 248$ J/(K • mol)

There is the same number of moles of gaseous chemicals on both sides of the equation. However, $SO_{2\,(g)}$ has more bonds than $O_{2\,(g)}$. Hence $\Delta S° > 0$.

$\Delta S° = \Sigma S°_{\text{products}} - \Sigma S°_{\text{reactants}}$

$\Delta S° = [(1\ \cancel{\text{mol}})(248\ \text{J/(K} \bullet \cancel{\text{mol}}))] - [(1\ \cancel{\text{mol}})(205\ \text{J/(K} \bullet \cancel{\text{mol}})) + (1\ \cancel{\text{mol}})(33\ \text{J/(K} \bullet \cancel{\text{mol}}))]$

$\Delta S° = [248\ \text{J/K}] - [238\ \text{J/K}]$

$\Delta S° = 10$ J/K (per mole of $SO_{2\,(g)}$ formed)

Assignment
18.4 pg. 810 #7 to 14

18.5: Gibbs Free Energy

Free Energy (*G*): - the amount of energy related to the entropy of the universe accounting for the dependency of a constant temperature $\left(\Delta S_{univ} = -\frac{\Delta G}{T}\right)$ or $\Delta G = -\Delta S_{\text{univ}}T$.

- also known as Gibbs Free Energy named after Willard Gibbs.
- **like enthalpy, $G_{\text{elements}} = 0$.**
- **when $\Delta S_{\text{univ}} > 0$, $\Delta G < 0$, the process is thermodynamically spontaneous.**

$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$ ($\Delta S_{\text{sys}} = \Delta S°$ - standard entropy at constant temperature and pressure)

$\left(-\frac{\Delta G}{T}\right) = \Delta S^\circ + \left(-\frac{\Delta H^\circ}{T}\right)$ (Substitute ΔS_{univ} with $-\frac{\Delta G}{T}$ and ΔS_{surr} with $-\frac{\Delta H^\circ}{T}$)

$T\left(-\frac{\Delta G}{T}\right) = T\Delta S^\circ + T\left(-\frac{\Delta H^\circ}{T}\right)$ (Multiply each term by T)

$-\Delta G = T\Delta S° - \Delta H°$ (Simplify and rearrange to $\Delta G = \Delta H° - T\Delta S°$)

Gibbs Free Energy

$$\Delta S_{univ} = -\frac{\Delta G}{T} \qquad \text{or} \qquad \Delta G = -\Delta S_{univ} T$$

$$\Delta G = \Delta H° - T\Delta S°$$

ΔG = Free Energy of the Universe (kJ/mol or J/mol)
ΔH = Enthalpy of the System (kJ/mol or J/mol) **T = Temperature (K)**
$\Delta S°$ = Standard Entropy the System (kJ/(K • mol) or J/(K • mol)]

When $\Delta S_{univ} > 0$, $\Delta G < 0$, the process is Thermodynamically Spontaneous
When $\Delta S_{univ} = 0$, $\Delta G = 0$, the System is at Equilibrium ($\Delta H° = T\Delta S°$)
When $\Delta S_{univ} < 0$, $\Delta G > 0$, the process is Thermodynamically Non-Spontaneous

Cases for Spontaneity ($\Delta G < 0$)

$\Delta H°$	$\Delta S°$	Thermodynamic Spontaneity (ΔG)
+ (Endothermic)	+ (More Random - Less Order)	Spontaneous at High T
+ (Endothermic)	− (Less Random - More Order)	Always Non-Spontaneous ($\Delta G > 0$)
− (Exothermic)	+ (More Random - Less Order)	Always Spontaneous ($\Delta G < 0$)
− (Exothermic)	− (Less Random - More Order)	Spontaneous at Low T

Example 1: Together, carbon monoxide gas from incomplete combustion along with hydrogen gas is known as syngas. This is because the reaction of $CO_{(g)}$ and $H_{2\,(g)}$ produced liquid methanol, which is commonly used in the production of fibres and plastic, as well as light fuel. The production of methanol from syngas also produces energy that can be used for generating power.

$$CO_{(g)} + H_{2\,(g)} \rightarrow CH_3OH_{(l)} \qquad \Delta H = -128.5 \text{ kJ/mol},\ \ \Delta S = -333 \text{ J/(K • mol)}$$

a. Determine whether the reaction is spontaneous at 30.0°C.
b. Calculate the temperature at which the reaction will be at thermodynamic equilibrium.
c. Comment on the spontaneity of this reaction if the temperature is above and below this equilibrium temperature.

a.
$\Delta H = -128.5$ kJ/mol
$\Delta S = -333$ J/(K • mol) $= -0.333$ kJ/(K • mol)
$T = 30.0°C = 303.15$ K
$\Delta G = ?$

$\Delta G = \Delta H° - T\Delta S°$
$\Delta G = (-128 \text{ kJ/mol}) - (303.15\ \cancel{\text{K}})(-0.333 \text{ kJ/(}\cancel{\text{K}} \text{ • mol))}$

$\Delta G = -27.1$ kJ /mol at 30.0°C
Since $\Delta G < 0$, the reaction is Spontaneous

b.
$\Delta G = 0$ at equilibrium
$\Delta H = -128.5$ kJ/mol
$\Delta S = -0.333$ kJ/(K • mol)
$T = ?$

$\Delta G = \Delta H° - T\Delta S°$ $0 = \Delta H° - T\Delta S°$ at equilibrium
$T\Delta S° = \Delta H°$

$$T = \frac{\Delta H°}{\Delta S°} = \frac{-128\ \cancel{\text{kJ/mol}}}{-0.333\ \cancel{\text{kJ}}/(\text{K} \bullet \cancel{\text{mol}})} = \mathbf{384.384\ K}$$

$T_{eq} = 111°C$

c. At $T > 111°C$, $\Delta G > 0$ because $-T\Delta S$ term will be <u>dominant</u> (bigger magnitude than $\Delta H°$). The reaction will be Non-Spontaneous.
At $T < 111°C$, $\Delta G < 0$ because $\Delta H°$ term will be <u>dominant</u> (bigger magnitude than $-T\Delta S$). The reaction will be Spontaneous.

Example 2: The molar heat of vaporization and its corresponding molar change in entropy of methanol is 35.2 kJ/mol and 104 J/(K • mol) respectively at 1 atm. Determine the theoretical boiling point of methanol. What is the % error if an experimental result of 66.4°C was reported?

$\Delta G = 0$ at boiling point
$\Delta H = 35.2$ kJ/mol
$\Delta S = 104$ J/(K • mol)
$\Delta S = 0.104$ kJ/(K • mol)
$T = ?$

$CH_3OH_{(l)} \rightarrow CH_3OH_{(g)}$ $\Delta H = 35.2$ kJ/mol, $\Delta S = 104$ J/(K • mol)

$\Delta G = \Delta H° - T\Delta S°$ $0 = \Delta H° - T\Delta S°$ at equilibrium

$T\Delta S° = \Delta H°$

$$T = \frac{\Delta H°}{\Delta S°} = \frac{35.2\ \cancel{\text{kJ/mol}}}{0.104\ \cancel{\text{kJ}}/(\text{K} \bullet \cancel{\text{mol}})} = \mathbf{338.4615\ K}$$

Theoretical T_b = 65.3°C

$$\%\text{ error} = \frac{|\text{Theoretical} - \text{Experimental}|}{\text{Theoretical}} \times 100\% = \frac{|65.3°\text{C} - 66.4°\text{C}|}{65.3°\text{C}} \times 100\%$$

% error = 1.68%

Gibbs Free Energy and Chemical Reactions

Free Energy of a Chemical Reaction

$$\Delta G° = \Delta H° - T\Delta S° \quad \text{or} \quad \Delta G° = \Sigma G°_{products} - \Sigma G°_{reactants}$$

$\Delta G°$ = Standard Change in Free Energy of a System
$\Sigma G°_{products}$ = Total Standard Free Energy of all Products
$\Sigma G°_{reactants}$ = Total Standard Free Energy of all Reactants

Example 3: Given that $2\ H_{2\,(g)} + O_{2\,(g)} \rightarrow 2\ H_2O_{(g)}$ has a $\Delta H = -484$ kJ and $\Delta S = -89.0$ J/K, determine the free energy for $\Delta G°$ of the given chemical equation at 25.0°C.

$\Delta H = -484$ kJ
$\Delta S = -89.0$ J/K $= -0.0890$ kJ/K
$T = 25.0°C = 298.15$ K
$\Delta G = ?$

$2\ H_{2\,(g)} + O_{2\,(g)} \rightarrow 2\ H_2O_{(g)}$ $\Delta H = -484$ kJ

$\Delta G = \Delta H° - T\Delta S° = (-484\text{ kJ}) - (298.15\ \cancel{\text{K}})(-0.089\text{ kJ}/\cancel{\text{K}})$

$\Delta G = -457$ kJ at 25.0°C
Since $\Delta G < 0$, the reaction is Spontaneous

Example 4: Given that $N_{2\,(g)} + 3\ H_{2\,(g)} \rightarrow 2\ NH_{3\,(g)}$ has the following thermodynamic values, determine $\Delta H°$, $\Delta S°$ and $\Delta G°$ of the given chemical equation at 25.0°C. At what temperature will the formation of ammonia at equilibrium?

Chemicals	$H°$ (kJ /mol)	$S°$ [J/(K • mol)]
$N_{2\,(g)}$	0	192
$H_{2\,(g)}$	0	131
$NH_{3\,(g)}$	–46	193

$\Delta H° = \Sigma H°_{products} - \Sigma H°_{reactants}$
$\Delta H° = [(2\ \cancel{\text{mol}})(-46\text{ kJ}/\cancel{\text{mol}})] - [(1\ \cancel{\text{mol}})(0\text{ kJ}/\cancel{\text{mol}}) + (3\ \cancel{\text{mol}})(0\text{ kJ}/\cancel{\text{mol}})] = \mathbf{-92\ kJ}$

$\Delta S° = \Sigma S°_{products} - \Sigma S°_{reactants}$
$\Delta S° = [(2\ \cancel{\text{mol}})(193\text{ J}/(\text{K} \bullet \cancel{\text{mol}}))] - [(1\ \cancel{\text{mol}})(192\text{ J}/(\text{K} \bullet \cancel{\text{mol}})) + (3\ \cancel{\text{mol}})(131\text{ J}/(\text{K} \bullet \cancel{\text{mol}}))]$
$\Delta S° = [386\text{ J/K}] - [585\text{ J/K}] = \mathbf{-199\ J/K}$

$\Delta H = -92$ kJ $\quad N_{2\,(g)} + 3\,H_{2\,(g)} \rightarrow 2\,NH_{3\,(g)} \quad \Delta H = -92$ kJ

$\Delta S = -199$ J/K $= -0.199$ kJ/K $\quad \Delta G = \Delta H° - T\Delta S° = (-92\text{ kJ}) - (298.15\ \cancel{\text{K}})(-0.199\text{ kJ}/\cancel{\text{K}})$

$T = 25.0°C = 298.15$ K

$\Delta G = -33$ kJ at 25.0°C

Since $\Delta G < 0$, the reaction is Spontaneous

ΔG = ? **T_{eq} = ?**

$\Delta G = \Delta H° - T\Delta S° \qquad 0 = \Delta H° - T\Delta S°$ at equilibrium

$T\Delta S° = \Delta H°$

$$T = \frac{\Delta H°}{\Delta S°} = \frac{-92\ \cancel{\text{kJ}}}{-0.199\ \cancel{\text{kJ}}/\text{K}} = \mathbf{462.312\ K} \quad \mathbf{T_{eq} = 169°C}$$

For the reaction to go forward, T must be kept below 169°C.

Example 5: Given the following data,

$$Fe_2O_{3\,(s)} + 3\,CO_{(g)} \rightarrow 2\,Fe_{(s)} + 3\,CO_{2\,(g)} \qquad \Delta G° = -31\text{ kJ}$$
$$3\,Fe_2O_{3\,(s)} + CO_{(g)} \rightarrow 2\,Fe_3O_{4\,(s)} + CO_{2\,(g)} \qquad \Delta G° = -63\text{ kJ}$$
$$Fe_3O_{4\,(s)} + CO_{(g)} \rightarrow 3\,FeO_{(s)} + CO_{2\,(g)} \qquad \Delta G° = -9\text{ kJ}$$

calculate the $\Delta G°$ for the reaction $FeO_{(s)} + CO_{(g)} \rightarrow Fe_{(s)} + CO_{2\,(g)}$

Since 1 mole of $Fe_{(s)}$ is found on the product side of the final equation, we must <u>divide the 1st equation by 2</u>.

$$\tfrac{1}{2}Fe_2O_{3\,(s)} + \tfrac{3}{2}CO_{(g)} \rightarrow Fe_{(s)} + \tfrac{3}{2}CO_{2\,(g)} \qquad \mathbf{\Delta G° = \frac{-31\text{ kJ}}{2} = -15.5\ kJ}$$

Because 1 mole of $FeO_{(s)}$ is located at the reactant side of the final equation, we must <u>flip the 3rd equation and divide it by 3</u>.

$$FeO_{(s)} + \tfrac{1}{3}CO_{2\,(g)} \rightarrow \tfrac{1}{3}Fe_3O_{4\,(s)} + \tfrac{1}{3}CO_{(g)} \qquad \mathbf{\Delta G° = \frac{-(-9\text{ kJ})}{3} = 3\ kJ}$$

Now we have to cancel out ½ mole of $Fe_2O_{3\,(s)}$ from the modified 1st equation. Hence, we must <u>flip the 2nd equation and divide it by 6</u>.

$$\tfrac{1}{3}Fe_3O_{4\,(s)} + \tfrac{1}{6}CO_{2\,(g)} \rightarrow \tfrac{1}{2}Fe_2O_{3\,(s)} + \tfrac{1}{6}CO_{(g)} \qquad \mathbf{\Delta G° = \frac{-(-63\text{ kJ})}{6} = 10.5\ kJ}$$

Now we add the equation and cancel equal moles of same chemicals found on both sides.

$$\cancel{\tfrac{1}{2}Fe_2O_{3\,(s)}} + \tfrac{3}{2}CO_{(g)} \rightarrow Fe_{(s)} + \tfrac{3}{2}CO_{2\,(g)} \qquad \mathbf{\Delta G° = -15.5\ kJ}$$
$$FeO_{(s)} + \tfrac{1}{3}CO_{2\,(g)} \rightarrow \cancel{\tfrac{1}{3}Fe_3O_{4\,(s)}} + \tfrac{1}{3}CO_{(g)} \qquad \mathbf{\Delta G° = 3\ kJ}$$
$$\cancel{\tfrac{1}{3}Fe_3O_{4\,(s)}} + \tfrac{1}{6}CO_{2\,(g)} \rightarrow \cancel{\tfrac{1}{2}Fe_2O_{3\,(s)}} + \tfrac{1}{6}CO_{(g)} \qquad \mathbf{\Delta G° = 10.5\ kJ}$$

$$FeO_{(s)} + CO_{(g)} \rightarrow Fe_{(s)} + CO_{2\,(g)} \qquad \mathbf{\Delta G° = -2\ kJ}$$

Spontaneous

$(\tfrac{3}{2}CO_{(g)} - (\tfrac{1}{3}CO_{(g)} + \tfrac{1}{6}CO_{(g)})$ yields 1 $CO_{(g)}$ on the reactant side)

$(\tfrac{3}{2}CO_{2\,(g)} - (\tfrac{1}{3}CO_{2\,(g)} + \tfrac{1}{6}CO_{2\,(g)})$ yields 1 $CO_{2\,(g)}$ on the product side)

<u>Assignment</u>

18.5 pg. 811−813 #17 to 20, 42, 44, 51, 52, 54, 56 to 61

Chapter 23: Nuclear Chemistry

23.1: The Nature of Nuclear Reactions

Nucleons: - the particles that make up a nucleus of an atom (**protons,($^{1}_{1}p^{+}$ or $^{1}_{1}$H) and neutrons, ($^{1}_{0}n$)**).

Isotopes: - atoms that have different mass number but the same atomic number or number of protons.

Nuclide: a particular atom or isotope containing specific numbers of protons and neutrons

Mass Number (# of p^{+} and n) → Atomic Number (# of p^{+}) →	$^{A}_{Z}X$	← Element Symbol (based on Atomic #)

Radioactivity: - the particles and/or electromagnetic radiation that are emitted due to unstable nuclei.
- all elements having atomic number 84 (Polonium) and greater are radioactive.

Nuclear Transmutation: - a process where radioactivity is resulted from the bombardment of nuclei by neutrons, protons or other nuclei.
- in most cases, heavier elements are synthesized from lighter elements.

History of Radioactivity

- In 1896, **Wilhelm Roentgen** discovered X-ray by examining ray emitting from the outside of the cathode ray glass tube. It has the capability of passing through solid materials, but can be blocked by denser matters. It can also be exposed to photographic plate, resulting from an image of "seeing through" an container made of less dense material.
- In the same year, **Antoine Becquerel** discovered that uranium emits a ray onto a photographic plate in the absence of sunlight or other forms of energy.
- A few years later, **Marie and Pierre Curie** demonstrated that radiation can be emitted by other elements. They discovered two new elements (polonium and radium) based on their tendency to emit radiation (**radioactivity**).

Types of Radioactive Particle and Decay

1. **Alpha Particle (α particle)**: - basically a helium nucleus (**$^{4}_{2}$He**), commonly found during radioactive decay from heavier nuclide (the net result is to **increase the neutron to proton ratio** – more explanation in the next section).

   Example: $^{218}_{84}\text{Po} \rightarrow\ ^{214}_{82}\text{Pb} +\ ^{4}_{2}\textbf{He}$

2. **Beta Particle (β particle)**: - basically an electron ($^{0}_{-1}e$ or $^{0}_{-1}\beta$) that is emitted when the neutron to proton ratio is higher than the zone of stability **(a neutron is transformed to a proton and an electron as a result** – more explanation in the next section**)**.
   - electrons have a mass number of 0 and an atomic number assignment of −1, due to its charge.

   Example: $^{214}_{82}\text{Pb} \rightarrow\ ^{214}_{83}\text{Bi} +\ ^{0}_{-1}e$ ($^{1}_{0}n \rightarrow\ ^{1}_{1}p +\ ^{0}_{-1}e$)

3. **Gamma Ray** (γ **ray**): - also known as a high-energy photon ($^{0}_{0}\gamma$) that is usually a by-product of an alpha-particle decay.
   - photon has no mass and no atomic number.

   Example: $^{238}_{92}\text{U} \rightarrow {}^{234}_{90}\text{Th} + {}^{4}_{2}\text{He} + 2\,{}^{0}_{0}\gamma$

4. **Positron** (e^+): - an antimatter of electron ($^{0}_{1}e$ **or** $^{0}_{1}\beta$) that is emitted when the neutron to proton ratio is lower than the zone of stability (**a proton is transformed to a neutron** as a result - more explanation in the next section).
   - positrons have a mass number of 0 and an atomic number of 1, due to its charge.
   - when a positron and an electron collide, they **annihilate** themselves to produce energy **(matter-antimatter reaction)**.

   Example: $^{15}_{8}\text{O} \rightarrow {}^{15}_{7}\text{N} + {}^{0}_{1}e$ $\quad$ $({}^{1}_{1}p \rightarrow {}^{1}_{0}n + {}^{0}_{1}e)$

5. **Electron Capture**: - an inner-orbital electron is "captured" by the nucleus to **increase neutron to proton ratio**. It is usually accompanied by an emission of gamma ray.

   Example: $^{73}_{33}\text{As} + {}^{0}_{-1}e \rightarrow {}^{73}_{32}\text{Ge} + {}^{0}_{0}\gamma$

Balancing Nuclear Equations: - the total atomic number (Z) and the total atomic mass (A) have to balance on both sides.

Example 1: Balance the following nuclear equations.

a. $^{222}_{86}\text{Rn}$ produces an α particle.

$^{222}_{86}\text{Rn} \rightarrow {}^{218}_{84}\textbf{Po} + {}^{4}_{2}\textbf{He}$ $\quad$ A: 222 = **(218)** + **(4)**, Z: 86 = **(84 → Po)** + **(2)**

b. $^{14}_{6}\text{C}$ produces a β particle.

$^{14}_{6}\text{C} \rightarrow {}^{14}_{7}\textbf{N} + {}^{0}_{-1}e$ $\quad$ A: 14 = **(14)** + **(0)**, Z: 6 = **(7 → N)** + **(–1)**

c. $^{49}_{21}\text{Sc}$ produces a β particle and a neutron.

$^{49}_{21}\text{Sc} \rightarrow {}^{48}_{22}\textbf{Ti} + {}^{0}_{-1}e + {}^{1}_{0}\textbf{n}$ $\quad$ A: 49 = **(48)** + **(0)** + **(1)**, Z: 21 = **(22 → Ti)** + **(–1)** + **(0)**

d. $^{11}_{6}\text{C}$ produces a positron.

$^{11}_{6}\text{C} \rightarrow {}^{11}_{5}\textbf{B} + {}^{0}_{1}e$ $\quad$ A: 11 = **(11)** + **(0)**, Z: 6 = **(5 → B)** + **(1)**

e. $^{40}_{19}\text{K}$ captures an electron to produce γ ray

$^{40}_{19}\text{K} + {}^{0}_{-1}e \rightarrow {}^{40}_{18}\textbf{Ar} + {}^{0}_{0}\gamma$ $\quad$ A: 40 + **(0)** = **(40)** + **(0)**, Z: 19 + **(–1)** = **(18 → Ar)** + **(0)**

f. $^{1}_{1}\text{H}$ reacts with $^{15}_{7}\text{N}$ to produce an α particle with γ ray.

$^{1}_{1}\text{H} + {}^{15}_{7}\text{N} \rightarrow {}^{12}_{6}\textbf{C} + {}^{4}_{2}\textbf{He} + {}^{0}_{0}\gamma$ $\quad$ A: 1 + 15 = **(12)** + **(4)** + **(0)**, Z: 1 + 7 = **(6 → C)** + **(2)** + **(0)**

g. $^{20}_{9}\text{F} \rightarrow {}^{20}_{10}\text{Ne} +$ ______

A: 20 = 20 + **(0)**, Z: 9 = 10 + **(–1)** } ${}^{0}_{-1}e$

$^{20}_{9}\text{F} \rightarrow {}^{20}_{10}\text{Ne} + {}^{0}_{-1}e$

h. $^{239}_{94}\text{Pu} +$ ____ $\rightarrow {}^{242}_{96}\text{Cm} + {}^{1}_{0}\text{n}$

A: 239 + **(4)** = 242 + 1, Z: 94 + **(2)** = 96 + 0 } ${}^{4}_{2}\textbf{He}$

$^{239}_{94}\text{Pu} + {}^{4}_{2}\textbf{He} \rightarrow {}^{242}_{96}\text{Cm} + {}^{1}_{0}\text{n}$

i. $^{54}_{27}\text{Co} \rightarrow$ ______ $+ {}^{0}_{1}e$

A: 54 = **(54)** + 0, Z: 27 = **(26 → Fe)** + 1

$^{54}_{27}\text{Co} \rightarrow {}^{54}_{26}\textbf{Fe} + {}^{0}_{1}e$

23.2: Nuclear Stability

Strong Nuclear Force: - a force of attraction that is present over extremely short distance (1×10^{-15} m) between all nucleons (protons and neutrons).
- it is much stronger than electromagnetic force in short distances. However, electromagnetic force is more significant over longer distances.

Properties of Neutrons:

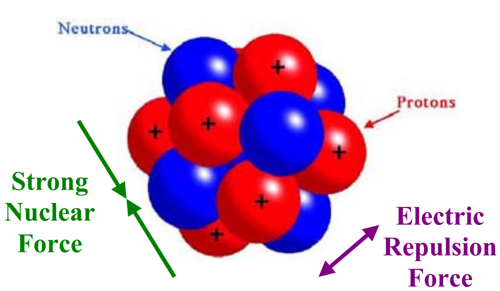
1. **Neutrons** serve as ***"nuclear cement"***, gluing neighbouring protons together despite the electric repulsion of positive charges, but only **over short distances**.

2. At large distances, strong nuclear force become less significant. Hence, **the MORE Protons in the nucleus (Heavier Atoms), the MORE Neutrons are needed to hold them together**. Sometimes this means for every 1 proton, there are 1.5 times to twice as many neutrons.

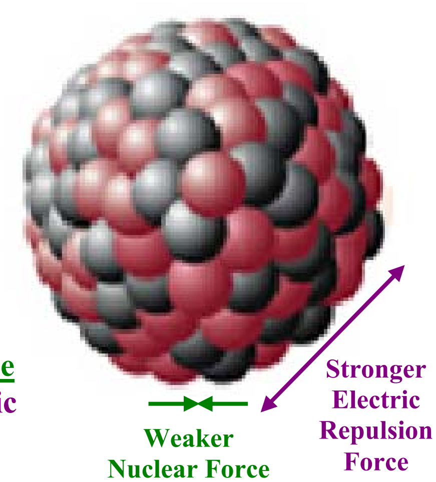
3. **SMALLER Atomic Nuclei usually have the SAME Number of Protons as Neutrons.**

4. **A Single Neutron is rather UNSTABLE. It will CONVERT itself to a Proton and an Electron.**

$${}^{1}_{0}n \rightarrow {}^{1}_{1}\text{H} + {}^{0}_{-1}e \rightarrow \text{(basically a hydrogen atom)}$$



For Small Nucleus, Strong Nuclear Force is MORE significant compared to electric repulsive force between protons due to small distances between nucleons.



For Large Nucleus, Electric Repulsive Force between Protons is MORE significant compared to strong nuclear force because of the large distances between nucleons. Hence, they are inherently unstable and likely undergo alpha decay (see below).

Radioactive Decay: - when a heavier nucleus loses nucleons to become a smaller but more stable nucleus. In the process, it gives off radiation products like alpha-, beta- particles and/or gamma rays.

Zone of Stability: - a graph that depicts the relationship between the number of neutrons versus the number of protons, and the area where there are stable nuclides.

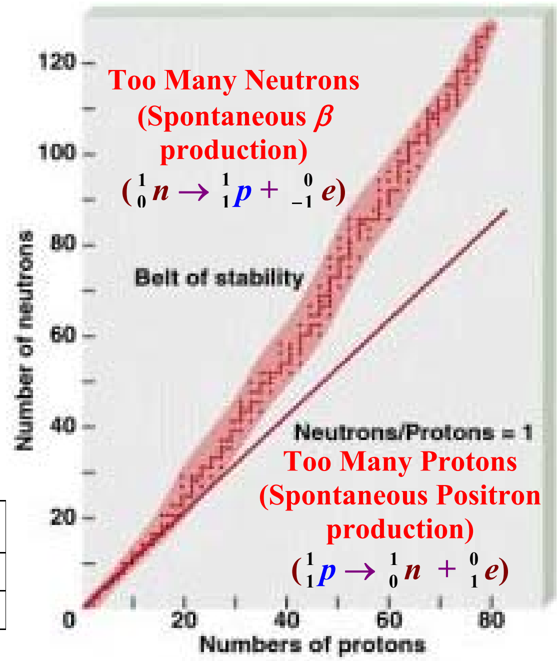
Common Observations of Radioactive Decay

1. When a nuclide has 84 or more protons ($Z \geq 84$), it tends to be **unstable** and likely undergo **radioactive decay**.
2. Lighter nuclides are stable when $Z = n$ (or $n : p^+$ ratio = 1). However, heavier nuclides are stable only when $Z < n$ (or $n : p^+$ ratio > 1).
3. Nuclides with **even # of p^+ with even # of n are more stable** than nuclides with odd # of p^+ and odd # of n.

   Example: Most Stable to Least Stable Nuclides
   ($^{12}_{6}C, ^{13}_{6}C, ^{19}_{9}F, ^{6}_{3}Li$)

Nuclide	$^{12}_{6}C$	$^{13}_{6}C$	$^{19}_{9}F$	$^{6}_{3}Li$
# of p^+	6 (even)	6 (even)	9 (odd)	3 (odd)
# of n	6 (even)	7 (odd)	10 (even)	3 (odd)

Stability: Most → Least



4. **Magic Numbers of protons or neutrons (2, 8, 20, 28, 50, 82 and 126) results in very stable nuclides**.

Thermodynamic Stability: - amount of potential energy inside a nucleus versus total potential energy of all nucleons.
- the difference in energy can be calculated using Einstein's equation ($\Delta E = \Delta mc^2$), where Δm is referred to as mass defect.

Mass Defect (Δm): - the change in masses during a nuclear transformation. **($\Delta m = m_{products} - m_{reactants}$)**
- sometimes masses for subatomic particles is measured in amu **(atomic mass unit)**
(1 kg = 6.022×10^{26} amu , or 1 g = 6.022×10^{23} amu = 1 mole amu).

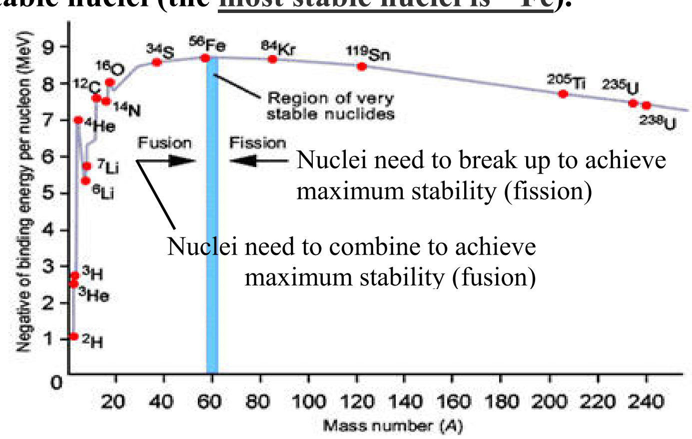
Subatomic Particle	Mass (kg)	Atomic Mass Unit (amu)
Neutron	1.67497×10^{-27}	1.008665
Proton	1.67357×10^{-27}	1.007825

Binding Energy (ΔE_{bind}): - the amount of energy released during a nuclear transformation because of a mass defect. It is used to bind the nucleons in the reactant nuclide.
- we often convert the unit to **electron volt (1 eV = 1.69×10^{-19} J or 1 MeV = 1.69×10^{-13} J).**
- **higher the ΔE_{bind} per nucleon means more mass is turned into pure energy to bind the nucleons together. Hence, bigger ΔE_{bind} means more stable nuclei (the most stable nuclei is ^{26}Fe).**

Einstein's Mass-Energy Conversion

$$\Delta E_{bind} = -\Delta mc^2$$

ΔE_{bind} = Binding Energy
Δm = mass defect (kg)
c = speed of light (3.00×10^8 m/s)



Example 1: Calculate the binding energy for carbon-13 (13.003355 amu) in J/nucleon and MeV/nucleon.

m of ${}^{13}_{6}C$ = 13.003355 amu

m of ($6p^+$ and $7n$) = 6(1.007825 amu) + 7(1.008665 amu) = 13.107605 amu

$\Delta m = m$ of ${}^{13}_{6}C - m$ of ($6p^+$ and $7n$) = 13.003355 amu − 13.107605 amu $\quad \Delta m = -0.104250$ amu

$$\Delta E = -\Delta mc^2 = -(-0.104250\ \cancel{\text{amu}})\left(\frac{1\ \text{kg}}{6.022\times10^{26}\ \cancel{\text{amu}}}\right)(3.00\times10^8\ \text{m/s})^2 = 1.5580372\times10^{-11}\ \text{J}$$

$$\Delta E_{\text{bind}}\text{ per nucleon} = \frac{1.5580372\times10^{-11}\ \text{J}}{13\ \text{nucleons}}$$

$$\Delta E_{\text{bind}} = 1.20\times10^{-12}\ \cancel{\text{J}}/\text{nucleon}\times\frac{1\ \text{MeV}}{1.69\times10^{-13}\ \cancel{\text{J}}}$$

$\Delta E_{\text{bind}} = 1.20 \times 10^{-12}$ J/nucleon

$\Delta E_{\text{bind}} = 7.09$ MeV/nucleon

Example 2: Calculate the energy released per mole of ${}^{235}_{92}U$ reacted when it undergoes nuclear fission:

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

(${}^{235}_{92}U$ = 235.0439 amu; ${}^{141}_{56}Ba$ = 140.9144 amu; ${}^{92}_{36}Kr$ = 91.9262 amu)

m_{initial} of ${}^{235}_{92}U + {}^{1}_{0}n$ = 235.0439 amu + 1.00899 amu = 236.05289 amu

m_{final} of ${}^{141}_{56}Ba + {}^{92}_{36}Kr + 3\,{}^{1}_{0}n$ = 140.9144 amu + 91.9262 amu + 3(1.00899 amu) = 235.86757 amu

$\Delta m = m_{\text{final}} - m_{\text{inital}}$ = 235.86757 amu − 236.05289 amu $\quad \Delta m = -0.18532$ amu

$$\Delta E = -\Delta mc^2 = -(-0.18532\ \cancel{\text{amu}})\left(\frac{1\ \text{kg}}{6.022\times10^{26}\ \cancel{\text{amu}}}\right)(3.00\times10^8\ \text{m/s})^2 = 2.76964464\times10^{-11}\ \text{J/nucleus}$$

$\Delta E_{\text{bind}} = 2.76964464\times10^{-11}$ J/~~nucleus~~ × (6.022 × 10^{23} ~~nucleus~~/mol) = 1.66788 × 10^{13} J/mol

$\Delta E_{\text{bind}} = 1.67 \times 10^{10}$ kJ/mol = 16.7 TJ/mol $\quad$ 1 TJ (Tera-Joules) = 1 × 10^{12} J

Assignment

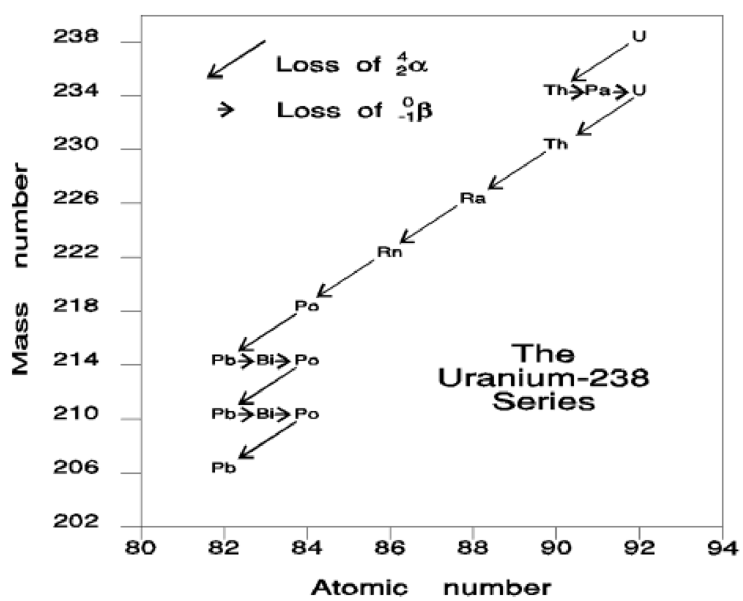
23.1 pg. 994–995 #1 to 6, pg. 996 #55

23.2 pg. 995 #7, 8, 11, 12, 14, 16, 18 to 20; pg. 998 #80

23.3: Natural Radioactivity

Decay Series: - a succession of decays from a particular radioactive nuclide until the formation of a stable nuclide.

Rate of Decay: - the rate at which a given radioactive nuclide decays over time.
- the negative of the change in the number of nuclides per unit of time (measured in reciprocal time unit).



Kinetic Stability: - sometimes called **radioactive decay** (a process where a nucleus decomposes into a different nucleus to achieve more stability).

Non-Calculus Explanation:

$N = N_0 e^{-kt}$ (Continuous Exp Decay)

$\frac{N}{N_0} = e^{-kt}$ (Solving for $-kt$)

$\ln\left(\frac{N}{N_0}\right) = \ln\left(e^{-kt}\right)$ (Natural log both sides)

$\ln\left(\frac{N}{N_0}\right) = -kt \ln e$ ($\ln e = 1$)

Derivation Using Calculus:

$Rate = -\frac{\Delta N}{\Delta t} = kN$ (**k = Rate Constant, N = Amount of Nuclide**)

$\frac{1}{N}\Delta N = -k\Delta t$ (Rearrange for Integration, $\Delta N = dN$; $\Delta t = dt$)

$\int_{N_0}^{N} \frac{1}{N}\,dN = -k\int_0^t dt$ (Integrate Both Sides: $\int \frac{1}{x}\,dx = \ln x$)

$\ln N - \ln N_0 = -kt$ (Use Logarithm Law: $\log A - \log B = \log\left(\frac{A}{B}\right)$)

$$\boxed{\ln\left(\frac{N}{N_0}\right) = -kt \qquad \textbf{(Radioactive Decay Equation)}}$$

Half-Life ($t_{½}$): - the amount of time it takes to half the amount of radioactive nuclides.
- at **half-life, $t_{½}$**, the amount of radioactive nuclides ½ $N_0 = N$:

$$\ln\left(\frac{N}{N_0}\right) = -kt \Rightarrow \ln\left(\frac{\left(\frac{1}{2}\cancel{N_0}\right)}{\cancel{N_0}}\right) = -kt_{½} \Rightarrow \ln(½) = -kt_{½} \Rightarrow \ln(2) = kt_{½}$$

$$t_{½} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

Radioactive Decay Equations

$$\ln\left(\frac{N}{N_0}\right) = -kt \qquad t_{½} = \frac{\ln 2}{k} = \frac{0.693}{k} \qquad N = N_0\left(\frac{1}{2}\right)^{\frac{t}{t_{1/2}}}$$

N = Amount of Nuclide at time t **N_0 = Amount of Nuclide at time 0**
k = Rate Constant (s^{-1}, min^{-1}, hr^{-1}, day^{-1}, yr^{-1}) **t = total decay time** **$t_{½}$ = half-life**

Example 1: Technetium-99, the first synthetic element in the Table, is used as a radiotracer for many organs such as heart, liver and lungs. It has a half-life of 6.0 hours. Draw a graph showing how 100 mg of ${}^{99}_{43}Tc$ decays over time. What is the radioactive amount of ${}^{99}_{43}Tc$ after 2.00 days?

$N_0 = 100$ mg
$t_{½} = 6.0$ hrs
$t = 2.00$ days $= 48.0$ hrs
$N = ?$

$$N = N_0\left(\frac{1}{2}\right)^{\frac{t}{t_{1/2}}}$$

$$N = (100 \text{ mg})\left(\frac{1}{2}\right)^{\frac{48.0\,\cancel{hrs}}{6.0\,\cancel{hrs}}}$$

$N = 0.391$ mg

$$t_{½} = \frac{\ln 2}{k} \qquad k = \frac{\ln 2}{t_{1/2}} \qquad k = \frac{\ln 2}{6\text{ hr}}$$

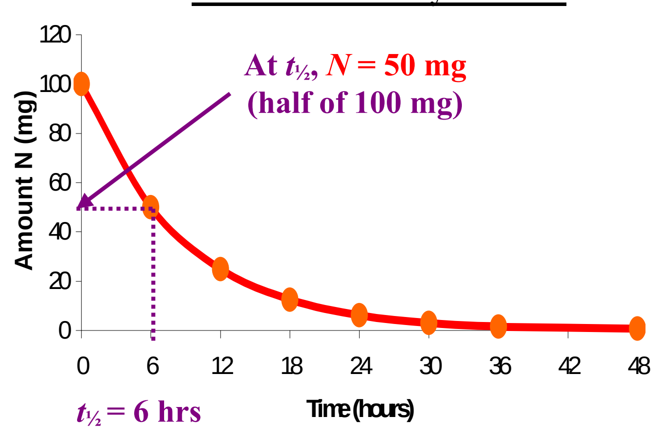
$$\ln\left(\frac{N}{N_0}\right) = -kt \qquad \frac{N}{N_0} = e^{-kt}$$

$$N = N_0\, e^{-kt}$$

$$N = (100\text{ mg})\,e^{-\frac{\ln 2}{6\,\cancel{hr}}(48.0\,\cancel{hr})}$$

$N = 0.391$ mg

Radioactive Decay of Tc-99



Example 2: ${}^{131}_{53}\text{I}$ is a radiotracer used to detect thyroid activity. The half-life of ${}^{131}_{53}\text{I}$ is 8.1 days.

a. Determine the rate constant of ${}^{131}_{53}\text{I}$.

b. How long will it take a patient to have her initial dosage of ${}^{131}_{53}\text{I}$ to decrease to 1.00 % of its initial value?

$t_{1/2}$ = 8.1 days
$\frac{N}{N_0}$ = 0.01

k = ?
t = ?

a. $t_{1/2} = \frac{\ln 2}{k}$ $\qquad k = \frac{\ln 2}{t_{1/2}}$

$k = \frac{\ln 2}{8.1\text{ days}}$ $\qquad$ **k = 0.086 day^{-1}**

b. $\ln\left(\frac{N}{N_0}\right) = -kt$

$$t = \frac{\ln\left(\frac{N}{N_0}\right)}{-k} = \frac{\ln(0.01)}{-\left(\frac{\ln 2}{8.1\text{ days}}\right)} = 53.815\text{ days}$$

t = 54 days

$$N = N_0\left(\frac{1}{2}\right)^{\frac{t}{t_{1/2}}} \rightarrow \frac{N}{N_0} = \left(\frac{1}{2}\right)^{\frac{t}{t_{1/2}}}$$

$\log\left(\frac{N}{N_0}\right) = \frac{t}{t_{1/2}}\log(½)$

$$\frac{t_{1/2}\log\left(\frac{N}{N_0}\right)}{\log\left(\frac{1}{2}\right)} = t$$

$$t = \frac{(8.1\text{ days})\log(0.01)}{\log(0.5)} = 53.815\text{ days}$$

t = 54 days

Example 3: ${}^{222}_{86}\text{Rn}$ is a natural alpha particle producer. Due to its noble gas characteristic, it can cause damage to tissues as it can be easily inhaled into the body. ${}^{222}_{86}\text{Rn}$ can be found quite easily in uranium mine because it is a decay product of ${}^{238}_{92}\text{U}$. In an analysis 50.0 mg ${}^{222}_{86}\text{Rn}$ decayed to 45.7 mg in 24.0 hours. Determine the half-life of ${}^{222}_{86}\text{Rn}$ and its rate constant.

N_0 = 50.0 mg
N = 45.7 mg
t = 24.0 hrs

$t_{1/2}$ = ?

k = ?

Solving k first:

$\ln\left(\frac{N}{N_0}\right) = -kt$

$$k = \frac{\ln\left(\frac{N}{N_0}\right)}{-t} = \frac{\ln\left(\frac{45.7\cancel{\text{mg}}}{50.0\cancel{\text{mg}}}\right)}{-24.0\text{ hrs}}$$

k = 0.00375 hr^{-1}

Then, solve for $t_{1/2}$:

$$t_{1/2} = \frac{\ln 2}{k} = \frac{\ln 2}{0.0037468628\text{ hr}^{-1}}$$

$t_{1/2}$ = 185 hours = 7.71 days

Solving $t_{1/2}$ first:

$$N = N_0\left(\frac{1}{2}\right)^{\frac{t}{t_{1/2}}} \rightarrow \frac{N}{N_0} = \left(\frac{1}{2}\right)^{\frac{t}{t_{1/2}}}$$

$\log\left(\frac{N}{N_0}\right) = \frac{t}{t_{1/2}}\log(½)$

$$t_{1/2} = \frac{t\log\left(\frac{1}{2}\right)}{\log\left(\frac{N}{N_0}\right)} = \frac{(24.0\text{ hrs})\log(0.5)}{\log\left(\frac{45.7\cancel{\text{mg}}}{50.0\cancel{\text{mg}}}\right)}$$

$t_{1/2}$ = 185 hours = 7.71 days

Then solve for k:

$t_{1/2} = \frac{\ln 2}{k}$ $\qquad k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{185\text{ hrs}}$

k = 0.00375 hr^{-1}

Radiocarbon Dating: - sometimes called **carbon-14 dating**. ${}^{14}_{6}\text{C}$ can be found naturally in organic material and the atmosphere. It decays as soon as the organism dies (${}^{14}_{6}\text{C} \rightarrow {}^{0}_{-1}e + {}^{14}_{7}\text{N}$).

- uses the known ratio of ${}^{14}_{6}\text{C}/{}^{12}_{6}\text{C}$ of similar organic sample of the day with the ratio in the artefact and the half-life of ${}^{14}_{6}\text{C}$ being 5730 years to determine the age of the artefact.

Example 4: An ancient wooden artefact found in China has a $^{14}_{6}C$ decay rate of 5.2 counts per minute per gram of carbon. A comparison to a freshly cut piece of wood has a count of 13.6 counts per minute per gram of carbon. Given the rate of carbon-14 decay is 5730 years, determine the age of this artefact.

$$\frac{\text{Final Rate at } t}{\text{Initial Rate at } t = 0} = \frac{\cancel{k}N}{\cancel{k}N_0} = \frac{5.2\ \cancel{\text{counts}}/(\cancel{\text{min}} \bullet \cancel{\text{g}})}{13.6\ \cancel{\text{counts}}/(\cancel{\text{min}} \bullet \cancel{\text{g}})} \qquad t_{½} = 5730 \text{ yrs} \qquad t = ?$$

First, we solve for *k*.

$$t_{½} = \frac{\ln 2}{k} \quad \rightarrow k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{5730 \text{ yrs}} \qquad \mathbf{k = 1.209680943 \times 10^{-4}\ yr^{-1}}$$

Next, we solve for *t*.

$$\ln\left(\frac{N}{N_0}\right) = -kt \quad \rightarrow \quad t = \frac{\ln\left(\frac{N}{N_0}\right)}{-k} = \frac{\ln\left(\frac{5.2}{13.6}\right)}{-\left(\frac{\ln 2}{5730 \text{ yrs}}\right)} = 7947.642495 \text{ yrs} \qquad \mathbf{t = 7948\ years}$$

Uranium-238 Dating: - due to its lengthy half-life (4.5×10^9 years), it is used to date rocks and other ancient inorganic material. $^{238}_{92}U/^{206}_{82}Pb$ ratio is used as $^{238}_{92}U$ eventually decays to stable $^{206}_{82}Pb$.

$$^{238}_{92}U \rightarrow {}^{206}_{82}Pb + 8\ {}^{4}_{2}He + 6\ {}^{0}_{-1}e \qquad t_{½} = 4.51 \times 10^9 \text{ years}$$

Example 5: A piece of ore containing $^{238}_{92}U$ and $^{206}_{82}Pb$ was found. The ratio between $^{206}_{82}Pb$ to $^{238}_{92}U$ is 0.432. Suppose that no $^{206}_{82}Pb$ was originally present. Determine the age of the ore given that the half-life of $^{238}_{92}U$ is 4.5×10^9 years.

$$\frac{N \text{ of } {}^{206}_{82}\text{Pb at } t}{N \text{ of } {}^{238}_{92}\text{U at } t} = 0.432 = \frac{432}{1000} \Rightarrow \frac{N}{N_0} = \frac{N \text{ of } {}^{238}_{92}\text{U still present}}{N \text{ of } {}^{238}_{92}\text{U before}} = \frac{{}^{238}_{92}\text{U now}}{{}^{238}_{92}\text{U} + {}^{206}_{82}\text{Pb}} = \frac{1000}{1000 + 432} = \frac{1000}{1432}$$

$t_{½} = 4.5 \times 10^9$ yrs $\qquad t = ?$

First, we solve for *k*.

$$t_{½} = \frac{\ln 2}{k} \quad \rightarrow \quad k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{4.5 \times 10^9 \text{ yrs}} \qquad \mathbf{k = 1.54032707 \times 10^{-10}\ yr^{-1}}$$

Next, we solve for *t*.

$$\ln\left(\frac{N}{N_0}\right) = -kt \quad \rightarrow \quad t = \frac{\ln\left(\frac{N}{N_0}\right)}{-k} = \frac{\ln\left(\frac{1000}{1432}\right)}{-\left(\frac{\ln 2}{4.5 \times 10^9 \text{ yrs}}\right)} = 2{,}331{,}141{,}717 \text{ yrs} \qquad \mathbf{t = 2.3\ billion\ years}$$

Potassium-40 Dating: - used mainly in geochemistry to determine the age a metal ores. Its main mode of decay via electron capture $^{40}_{19}K$ turns it into $^{40}_{18}Ar$ with a half-life of 1.2×10^9 years. Using a mass spectrometer, we can easily measure the amount of $^{40}_{18}Ar$ trapped inside the lattice mineral. By calculating the $^{40}_{18}Ar$ / $^{40}_{19}K$, we can determine the age of a metal ore.

$$^{40}_{19}K + {}^{0}_{-1}e \rightarrow {}^{40}_{18}Ar \qquad t_{½} = 1.2 \times 10^9 \text{ years}$$

Assignment

23.3 pg. 995 #21, 23 to 26, 28, 29; pg. 997−998 #66 to 68, 85

23.4: Nuclear Transmutation

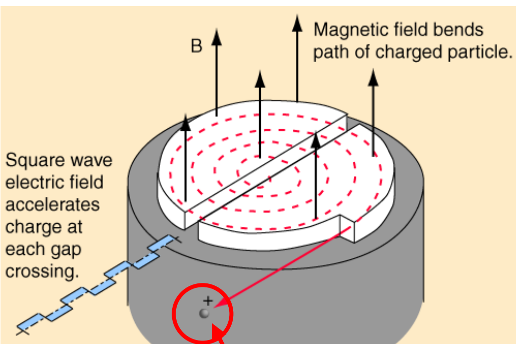
Nuclear Transmutation: - the reaction where one element is converted to another element by changing the number of protons.

Transuranium Elements: - elements that have been synthesized by nuclear transformation after the last natural element, uranium.

Example: $^{244}_{94}\text{Pu} + ^{48}_{20}\text{Ca} \rightarrow ^{289}_{114}\text{Uuq} + 3\ ^{1}_{0}\text{n}$ (Discovered in 1998 and $t_{1/2}$ = 30 seconds)

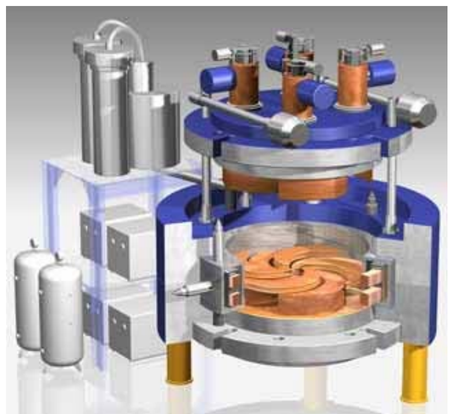
Particle Accelerator: - a device that alternates electric field to speed up a particle to add into a target nuclide.

a. **Cyclotron**: - a type of particle accelerator that utilizes a changing electric field along with a magnetic field to increase the speed of an ion around a disc before hitting a target nuclide.



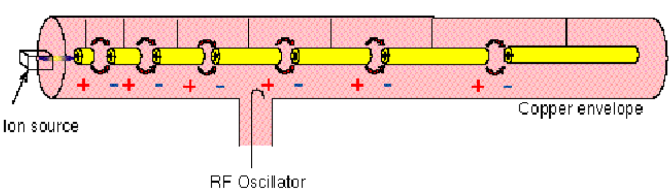
Schematic of a Cyclotron

Accelerated charged particle to collide with target nuclide



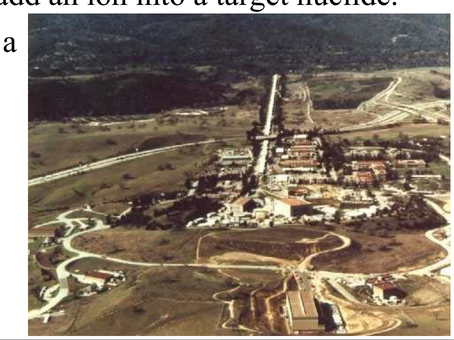
COMET: A medical superconducting cyclotron. It is used to generate thallium-201 (coronary arteries) and gallium-67 (soft-tissue tumors). It can also produce radio-pharmaceutical needed for PET and SPECT scans

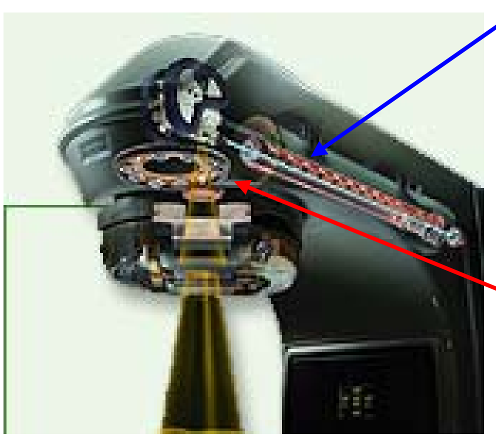
b. **Linear Accelerator**: - a particle accelerator that speeds up a particle by using an alternating electric field at different segment of a linear tube to add an ion into a target nuclide.



Left: Schematic of a Linear Accelerator

Right: Stanford Linear Accelerator



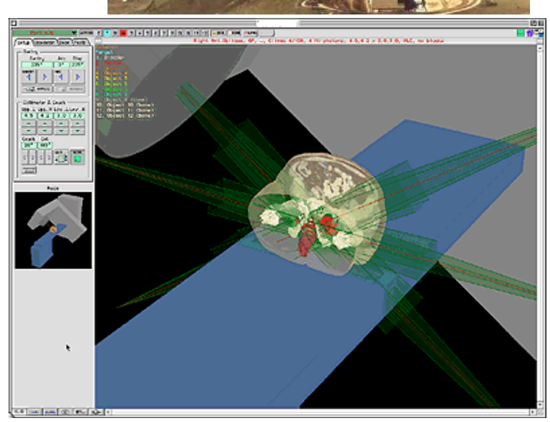


Linear Accelerator

Multileaf Collimeter to shape the beam

Schematic of a Medical Linear Accelerator

Computer Program is used to control radiotherapy treatment by a medical linear accelerator



Assignment
23.4 pg. 996 #33 to 36

23.5: Nuclear Fission

Nuclear Fission: - the breaking up of a heavier nucleus into two nuclei with small mass number.

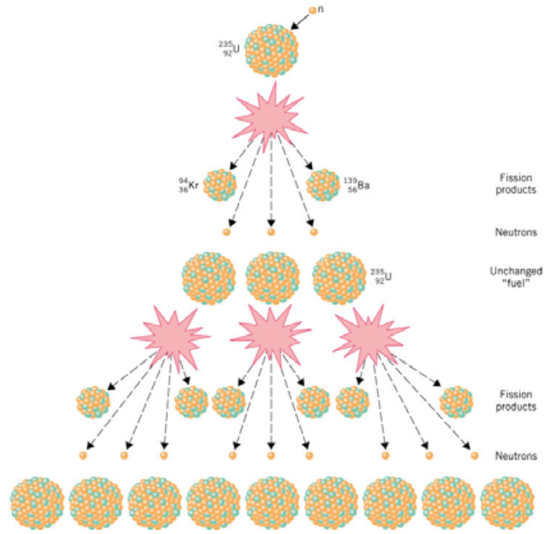
Example: $^{235}_{92}\text{U} + ^{1}_{0}\text{n} \rightarrow ^{141}_{56}\text{Ba} + ^{92}_{36}\text{Kr} + 3\,^{1}_{0}\text{n}$ $\Delta H = 2.0 \times 10^{10}$ kJ/mol

Chain Reaction: - when the nuclear fission is self-sustaining.

a. **Subcritical**: - when there is on average, less than one neutron produced per $^{235}_{92}\text{U}$ is consumed. The fission will eventually stop.

b. **Critical**: - when there is on average, exactly one neutron produced per $^{235}_{92}\text{U}$ consumed. The fission can then be self-sustaining at the same level.

c. **Supercritical**: - when there is one average, more than one neutron produced per $^{235}_{92}\text{U}$ is consumed. The fission can increase its rate rapidly and a violent explosion can result.



Critical Mass: - the minimum mass of fissionable material required for the generation of a self-sustaining nuclear chain reaction.

Spontaneous Fission: - when a heavy nuclide splits into two lighter nuclides and sometimes neutrons.

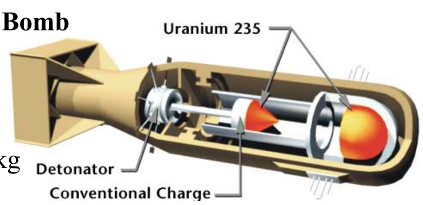
Example: $^{256}_{100}\text{Fm} \rightarrow ^{140}_{54}\text{Xe} + ^{112}_{46}\text{Pd} + 4\,^{1}_{0}\text{n}$

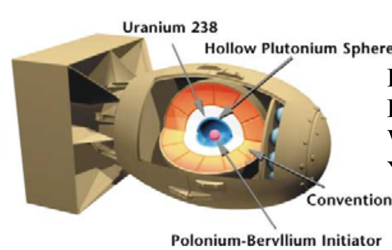
Atomic Bomb: - an uncontrolled nuclear fission device that releases large amount of energy.

- in 1939, just before WWII, Einstein and other scientists wrote to President Roosevelt that Nazi Germany was researching ways to purify U-235 for the purpose of an atomic bomb. This led to the US initiation of the "Manhattan Project" (a secret project to develop the atomic bomb by the US).
- the first atomic bomb test was conducted at Jemez Mountains in northern New Mexico on July 16, 1945 at 5:29:45 AM (Mountain War Time). Less than a month later, an atomic bomb (code name: Little Boy) was dropped on Hiroshima, Japan on Aug 6. It had a yield of 15 kilotons of TNT (6×10^{10} kJ ≈ 750 g of U-235) and it killed an estimated 80,000 people with 60,000 died later of radiation poisoning. Three days later, another atomic bomb (code name: Fat Man) was dropped on Nagasaki. It had a yield of 21 kilotons of TNT (8×10^{10} kJ ≈ 1 kg of Pu-239) and killed 74,000 people with several hundred thousands died from disease due to radiation.
- the "gun-type assembly" design detonation starts with conventional TNT explosion at one end of the device, pushing half the U-235 / Pu-239 subcritical mass into another half of the U-235 / Pu-239 subcritical mass located at the other end of the bomb. When the two masses connect, a supercritical chain reaction takes place and releases a large amount of heat energy. The "implosion" design involves detonate surrounding TNT to ignite a nuclear fission core.

Uranium "Gun" Atomic Bomb (Little Boy)

Length: 10 ft / 3 m
Diameter: 28 in / 71.1 m
Weight: 9,700 lbs / 4,400 kg
Yield: 15 kilotons



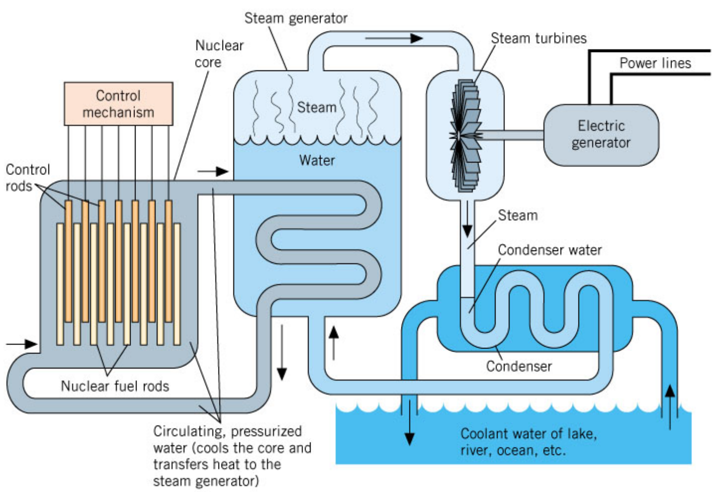


Plutonium Implosion Atomic Bomb (Fat Man)

Length: 10.7 ft / 3.25 m
Diameter: 5 ft / 1.5 m
Weight: 10,265 lbs / 4,656 kg
Yield: 21 kilotons

Nuclear Reactors: - fission reactors where enriched $^{235}_{92}U$ is placed in the **reactor core**. The heat is generated in the reactor is used to heat water. This water also acts as the moderator (a substance that slows down neutrons emitted and reduces their kinetic energy). **Control rods (usually made of carbon, cadmium, or boron to absorb extra neutrons)** can be lifted or lowered to control the rate of the fission process. The super-heated moderator water from the reactor core heats another tank of water, but the moderator water is recycled back into the reactor. As the water in the tank is heated into steam, it turns the steam turbine to generate electricity. This water is then cooled in a cooling tower and recycled (the hot water cannot be discharged into nearby lake or stream to avoid thermal pollution). Since large amount of cold water is needed for the cooling process of steam, most nuclear power plants are built near a large river or lake.

- the by-products of $^{235}_{92}U$ fission have a very long half-lives and can remain radioactive for a long time. Great efforts are needed to dispose of the wastes properly. The danger of a nuclear meltdown is also a constant danger as in the cases of Three Mile Island, Pennsylvania in 1979 and Chernobyl, Ukraine in 1986.



Bruce Power Nuclear Plant at Tiverton (Lake Huron), Canada

Light Water Reactor: - uses light water (regular H_2O) as moderator.
- all US nuclear reactors are light-water reactors and they use cadmium or boron control rods.
- since light water is a good absorber of neutrons, the uranium fuel used has to be enriched (the same initial process is used to make weapon-grade uranium, ^{235}U).

Heavy Water Reactor: - uses heavy water (D_2O – deuterium water - $^{2}_{1}H_2O$) as moderator.
- D_2O dose not absorb neutrons as well as H_2O (it has a neutron in the hydrogen atom already). Hence, the nuclear reactor is more efficient (more neutrons are left to do more fission collisions). As a result, uranium enrichment is not necessary. This eliminates the potential of a country to develop nuclear weapons.
- D_2O can be expensive to produce due to the amount of water needed for operating a nuclear power plant. Currently, Canada is the only country that uses heavy water reactor (CANDU reactor).

Breeder Reactor: - due to the limited resources of enriched uranium $^{235}_{92}U$, the excess neutrons in the fission reactor can be used to convert uranium-238 to plutonium-239 to be used as an alternate nuclear fuel.

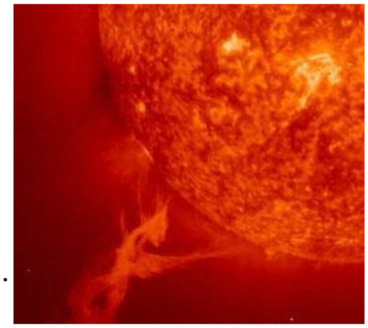
$$^{238}_{92}U + ^{1}_{0}n \rightarrow ^{239}_{94}Pu + 2\ ^{0}_{-1}e$$

- it is the most expensive type of reactor due to the its technical aspects. Currently, only Russia and France have a handful of breeder reactors.

23.6: Nuclear Fusion

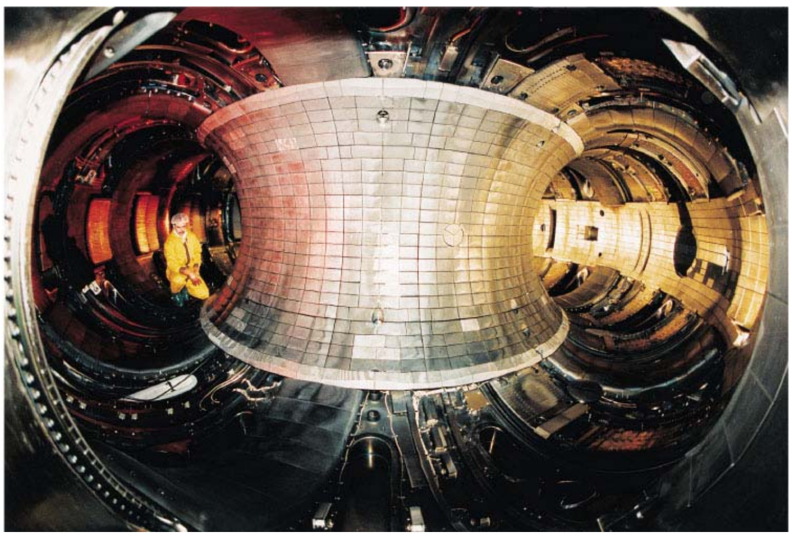
Nuclear Fusion: - the combining of two light nuclei into a heavier and more stable nucleus.

Example: $^{2}_{1}H + ^{3}_{1}H \rightarrow ^{4}_{2}He + ^{1}_{0}n$ $\Delta H = 1.7 \times 10^{9}$ kJ/mol

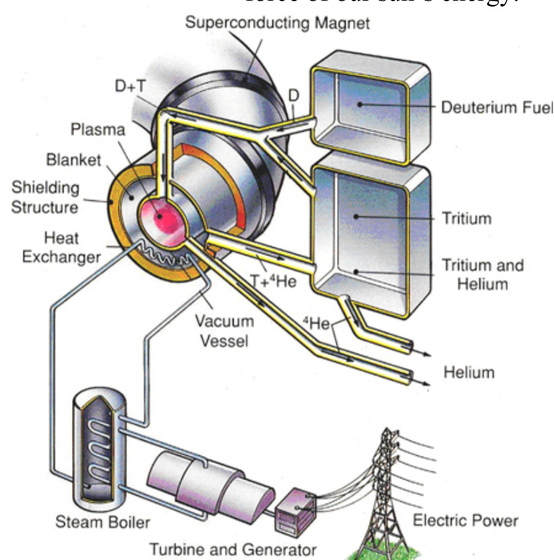


Fusion reaction is the driving force of our sun's energy.

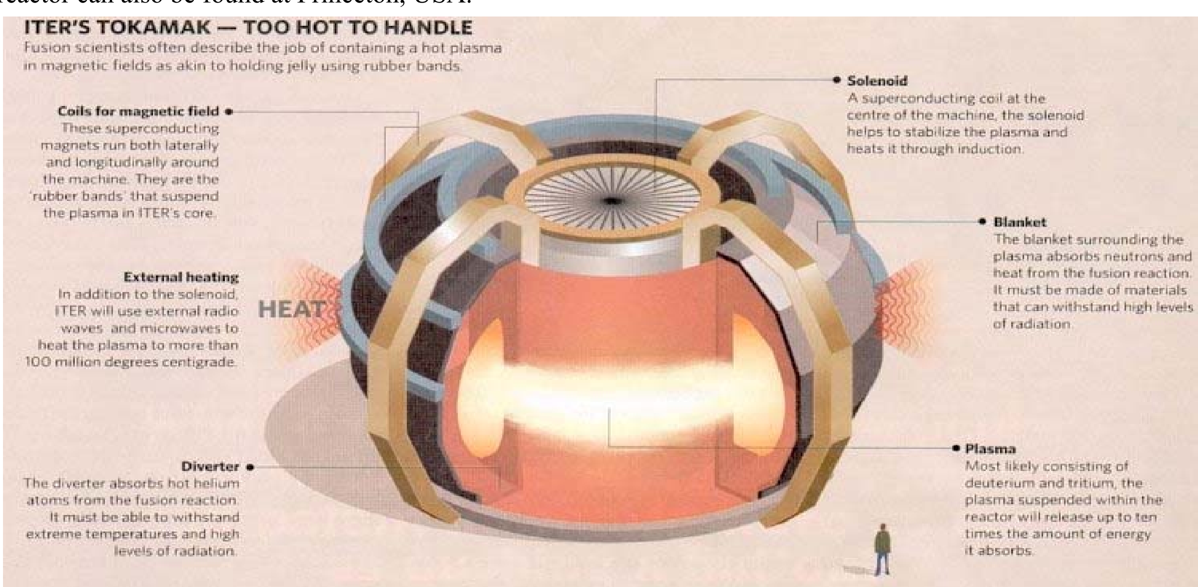
- the availability of hydrogen isotopes, deuterium ($^{2}_{1}H$) and tritium ($^{3}_{1}H$), in sea water and the harmless product, $^{4}_{2}He$, makes nuclear fusion an environmental friendly alternative to generate power.
- however, fusion reactions such as the one above usually require an initial temperature above 4×10^{7} K to overcome the strong electrostatic repulsion between the two protons (the release of significant binding energy can only achieve when the distance between the two protons is approximately 10^{-15} m). High-powered laser and heating by electric currents are being studied as methods to attain this high temperature to initial a control fusion reaction.



European Tokamak Fusion Test Reactor Vacuum Vessel employs the design of a toroid with a super strength magnetic field to contain plasma without having it touch the wall of the reactor. A similar experimental fusion reactor can also be found at Princeton, USA.



Propose Schematic of a Fusion Reactor to Generate Electricity

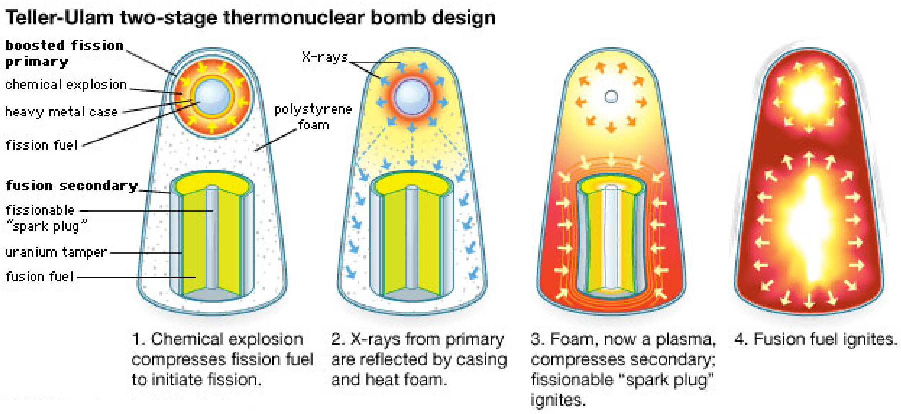


Hydrogen Bomb: - also called a thermonuclear bomb that uses fusion reaction to destroy a large target area.

- the device contains solid lithium deuteride (LiD or Li $^{2}_{1}$H) which can be packed tightly. The detonations involve a fission reaction to generate the initial heat to start the fusion reaction.

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

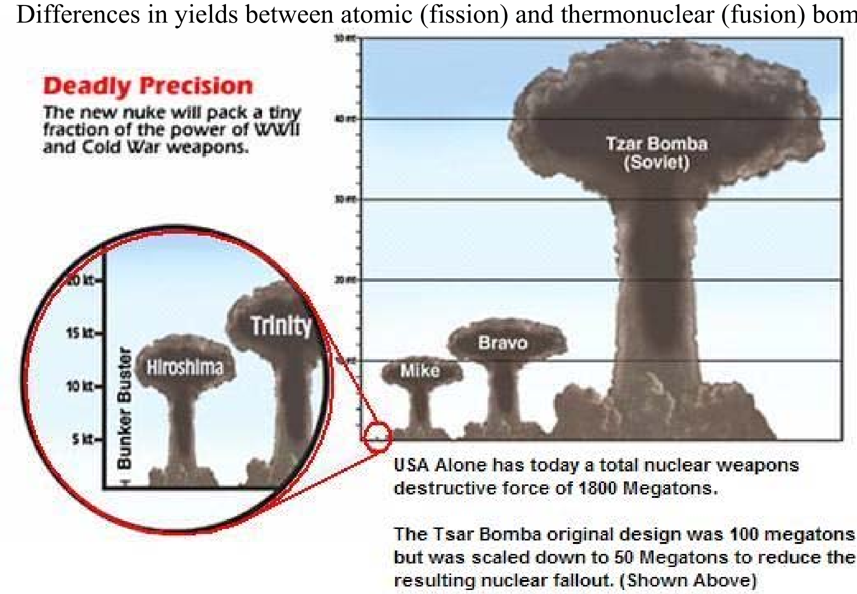
- fusion reaction is not limited by a critical mass as in fission reaction. Hence, the size of the explosion depends on the amount of fusion material.
- besides the intense heat to incinerate a large area, the damaging radiation effects come from the products of the fission starter and the product of the fusion reaction, tritium, has a half-life of 12.5 yrs. However, other radioactive material with longer half-life, such as Co-59, can be used to spread harmful radiations.

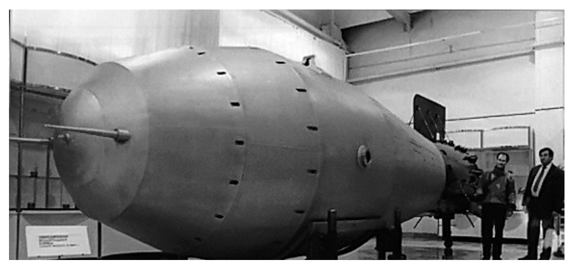


Thermonuclear Hydrogen Bomb (Teller-Ulam)

Length: 18.8 ft / 5.7 m
Diameter: 5 ft / 1.5 m
Weight: 39,600 lbs / 18,000 kg
Yield: 13.5 megatons

Differences in yields between atomic (fission) and thermonuclear (fusion) bombs





Thermonuclear Hydrogen Bomb (Tsar Bomba)

Length: 26.6 ft / 8 m Weight: 59,400 lbs / 27,000 kg
Diameter: 6.6 ft / 2 m Yield: 50 megatons
Tested on Oct 30, 1961at Novaya Zemlya Island, (north of the Russia)

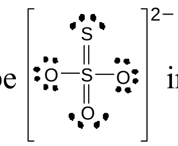
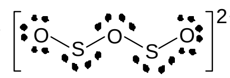
See Tsar Bomba explosion:
http://www.youtube.com/watch?v=FfoQsZa8F1c and
http://www.youtube.com/watch?v=BmQIkDkZ7sk

Assignment
23.5 & 23.6 pg. 996 #38, 40, 41, 44 to 46

23.7 & 23.8: Uses of Isotopes & Biological Effects of Radiation

Some Uses of Isotopes:

1. **Structural Determination**: - when a molecular or polyatomic ion structure is difficult to determine, an isotope of an element in the chemical can be used to study the mechanism of decomposition. This in addition of Infrared Spectral Analysis, we can determine the correct chemical structure of otherwise an ambiguous scenario.

   Example: Using ${}^{35}_{16}S$, thiosulfate, $S_2O_3^{2-}$ is determined to be  instead of .

Radioactive Tracers: - radioactive elements that leave a path of radiation that can be imaged to determine how the material is taken up by an organism.

2. **Study of Photosynthesis**: - radioactive tracers like ${}^{14}C$ and ${}^{18}O$ can be included in determine the path of carbon and oxygen during the process of photosynthesis and other nutrient uptakes

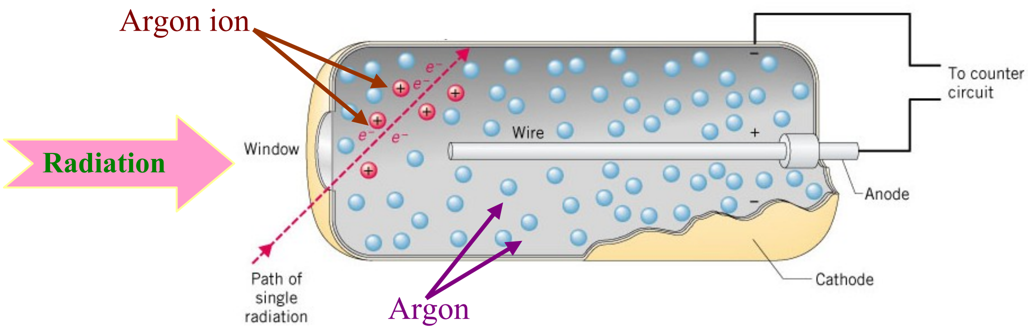
3. **Isotopes in Medicine**: - compound that contain a radioactive tracer (**carrier compound**), can be introduced to a patient. An device that can pick up radiation produces an image for the purpose of diagnosis (**medical imaging**).

Some Common Radioactive Tracers and their Usages:

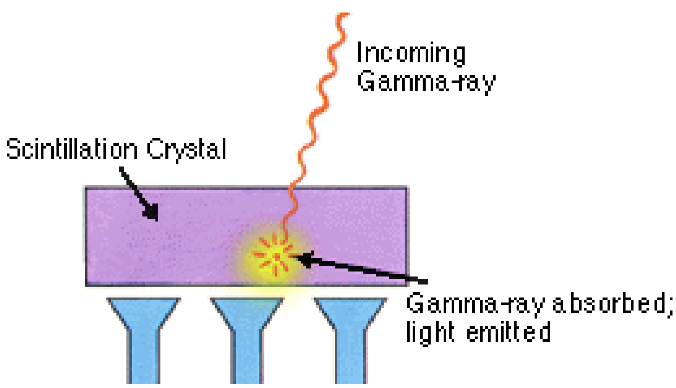
Radiotracers	Area of the Body Examine / Treatment	Other Usages
${}^{131}_{53}I$	Thyroid	
${}^{59}_{26}Fe$ and ${}^{51}_{24}Cr$	Red Blood Cells, Metabolism	Metallic Welds, Corrosion Mechanisms, Engine Wears
${}^{252}_{98}Cf$	Cervical and Brain Cancer Treatments	Detections of Metal Fatigue and Explosives
${}^{32}_{15}P$	Eyes, Liver, Tumours	Path and Rate of Adsorption of Plant Nutrients
${}^{60}_{27}Co$	Radiation Source of Radiotherapy	Food Irradiation, Sterilization of Medical Equipment
${}^{192}_{77}Ir$	Localize Prostate and Cervical Cancer Treatments	Metal Integrity Tests
${}^{87}_{38}Sr$ and ${}^{47}_{20}Ca$	Bones	
${}^{99}_{42}Mo$	Parent Generator of ${}^{99}_{43}Tc$	
${}^{99}_{43}Tc$	Brain, Myocardium, Thyroid, Lungs, Liver, Gallbladder, Kidneys, Skelton, Blood Flow and Tumours	Equipment Calibration and Nanoscale Nuclear Batteries
${}^{241}_{95}Am$		Smoke Detection
${}^{133}_{54}Xe$	Heart, Lungs, Brain and Blood Flow	
${}^{24}_{11}Na$	Extracellular Fluids, Circulatory System	Detection of Leaky Pipes

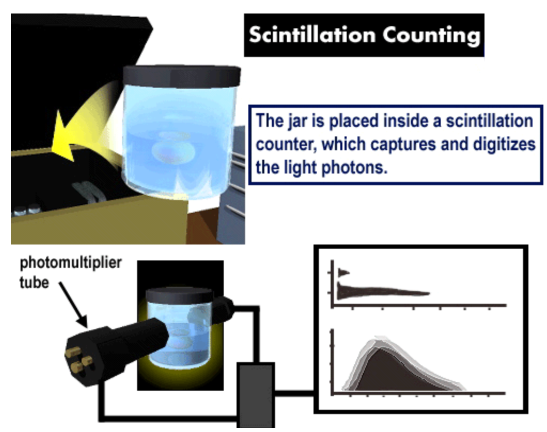
Detecting Radiations:

1. **Geiger-Müller Counter**: - sometimes refer to as the **Geiger Counter**. (Hans Geiger worked with Rutherford on his gold-foil experiment. The counter was invented to count the number of α-particles.)
   - argon gas becomes ionized and when struck by high-energy particle from radioactive decay. The resulting electric potential is amplified and the current can show as the intensity of the radioactivity.



2. **Scintillation Counter**: - zinc sulfide and other substances give off light when struck by high-energy particle from radioactive decay. A photocell measures the intensity of the light produced and gives the measure as the number of decay events per unit of time.





Radiation Damages: - high-energy particles generated by nuclear decays can cause damage to organisms. Depending on the doses, it can be shown either immediately or years after exposure.

a. **Somatic Damage**: - radiation damage to the organism's tissues or cell structures causes sickness or death.

Examples: Sunburn, hear rash, cancer, and cataracts

b. **Genetic Damage**: - radiation damage to the genetic code or reproduction process of the organism, which causes mutations in the offspring.

Examples: Genetic and DNA mutations

Sources of Radiation:

1. **Natural Radiations**: - small amounts of radiation happened naturally from the environment.
- **Cosmic radiation** from outer space and the sun (amounts vary by elevation from sea level).
- **Ground radiation** from Earth's interior that is responsible from heat of hot springs and geyser to the molten core of the planet. It is also present in organic food and water, building material such as bricks and wood products.
- **Air radiation** from randon-222 (inert gas from natural uranium deposits); easily inhale from basement cracks. Randon-222 is also found in tobacco smoke (man-made radiation).
- **Human tissues** contains about 20 mg of potassium-40 that emit pulses of radioactivity over time.

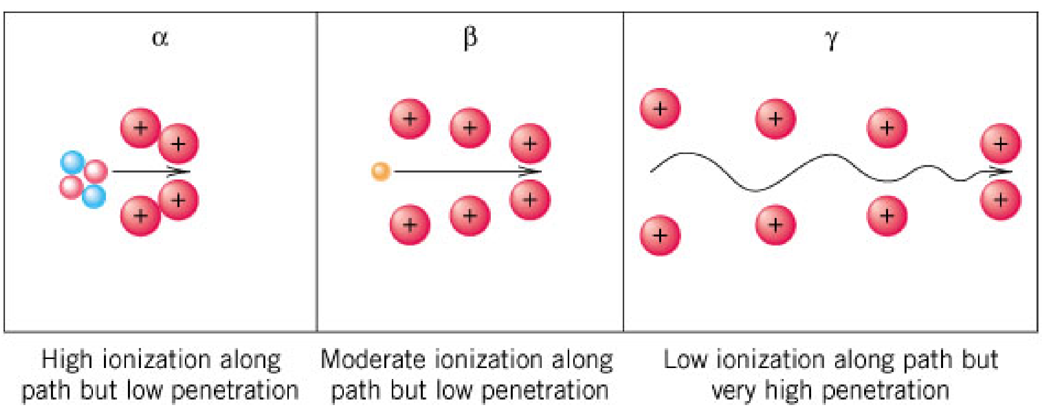
2. **Man-Made Radiations**: - radiations that are artificially created (intentional and unintentional).
- **Medical procedures** such as X-ray and radiotherapy and radio-diagnostic procedures.
- **Consumer products** like television tubes.
- **Proximity to Power Generators** like nuclear and coal power plants.
- **Aviation** from airline travels.
- **Nuclear Weapon Testing Fallouts** can travel all around the globe.

Biological Effects from Radiation

1. **Radiation Energy Level**: - **the higher the energy levels (doses), the more the severe are the damages**.
   - radiation doses are measured in *rads* (*r*adiation *a*bsorbed *d*oses – now an obsolete unit), 1 rad = 10 mJ.
   - ***rems*** (*r*oentgen *e*quivalent in *m*an), measures the ability to radiation to cause harm biologically.
   - it takes 500 rems to be considered lethal radiation dosage if it was given in a short period of time.
   - smaller radiation on a body can be measured in ***millirems***. (1000 millirems = 1 rem)

2. **Penetrating Ability**: - the lighter the particles, the more penetrating they can be. In terms of penetrating ability: **γ ray is the strongest, follows by β particles and α particle is the least penetrating.**

3. **Ionization Ability**: - as high-energy particles pass through tissue, it can cause ionization that is damaging to the organism. **α particles ionize the most along its path whereas γ ray does not.** Therefore, α particle producers like plutonium and radon can cause severe radiation damage if ingested or inhaled.



4. **Radiation Source's Chemical Properties**: - the length of the half-life of a radioactive nuclide can also affect radiation damage. Generally, **the longer the half-life, the more damage it can cause**. This is because it can reside in the organism for a longer period of time. This is why most radiotracers used in medical diagnosis have half-lives that are at most in days.

Assignment
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