

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.

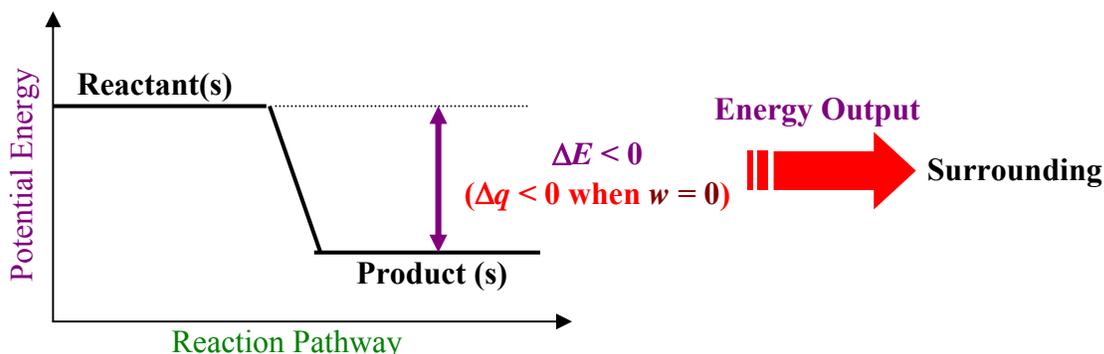
Open System: - a system where **mass and energy can interchange** freely with its surrounding.

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.

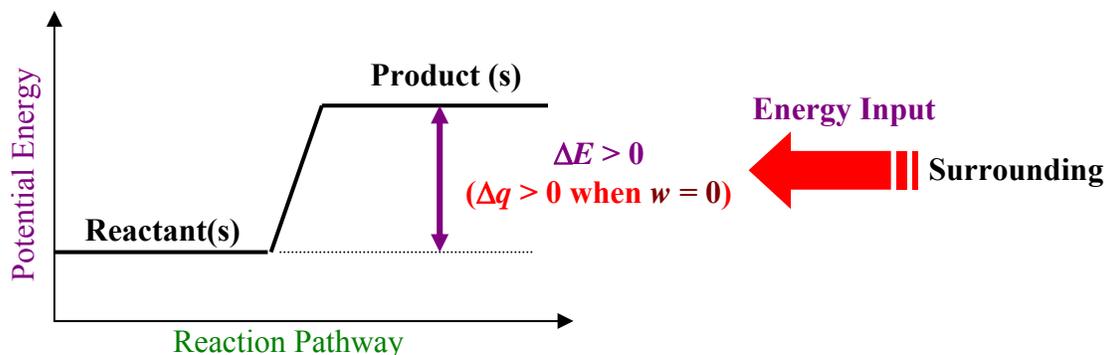
Exothermic Process ($\Delta E < 0$): - when energy flows “out” of the system into the surrounding.
(Surrounding gets Warmer.)

Potential Energy Diagram for Exothermic Process



Endothermic Process ($\Delta E > 0$): - 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** (ΔE) 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**).

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

$$w = (PA) \times \Delta d \quad (\text{Substitute } PA \text{ as Force; } A \times \Delta d = \text{Volume} - 3 \text{ dimensions})$$

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

$$w = -P \Delta V$$

(1 L • atm = 101.3 J)

Assignment

6.1 to 6.3 pg. 198 #1 to 3, 6 to 11

6.4: Enthalpy of Chemical Reactions

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

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

$$\Delta H - P \Delta V = q - P \Delta V \quad (\text{Equate } \Delta E \text{ and simplify by cancelling } -P \Delta V \text{ on both sides})$$

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

Change in Enthalpy in a Chemical Reaction

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

$\Delta H > 0$ Endothermic Reaction

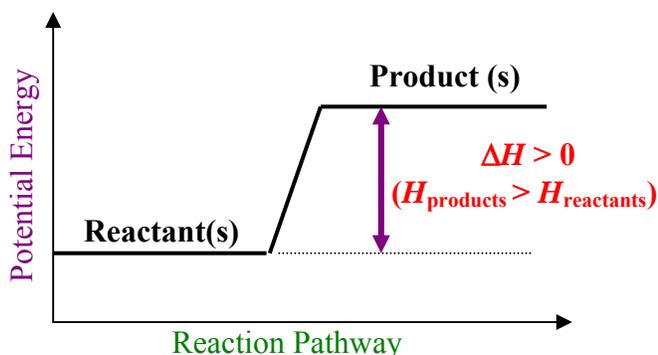
$\Delta H < 0$ Exothermic Reaction

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

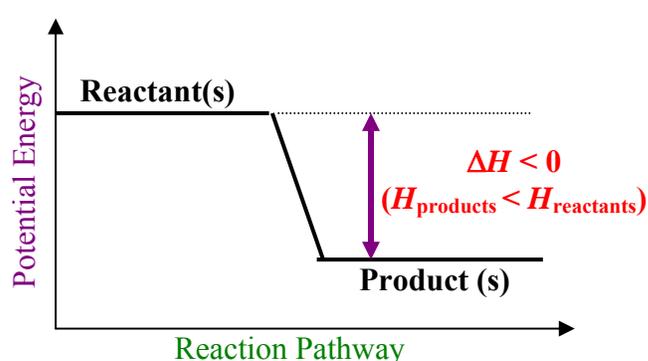
ΔH = Change in Enthalpy n = moles

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

Example: Water is vaporized from its liquid state.

b. Exothermic Reactions / Processes

Example: Methane undergoes combustion at constant pressure.



Example 1: It takes 116.2 kJ to form 84.0 L of $\text{NO}_2(g)$ from its elements at 1.00 atm and 25.0°C. Determine the molar heat of enthalpy for the formation of $\text{NO}_2(g)$. Express the answer in proper ΔH notation.

$$\begin{aligned} \Delta H &= 116.2 \text{ kJ} \\ V &= 84.0 \text{ L} \\ P &= 1.00 \text{ atm} \\ T &= 25.0^\circ\text{C} = 298.15 \text{ K} \\ R &= 0.0821 \frac{\text{atm}\cdot\text{L}}{\text{mol}\cdot\text{K}} \\ n &=? \quad \Delta H_{\text{rxn}} = ? \end{aligned} \quad \begin{aligned} n &= \frac{PV}{RT} = \frac{(1.00 \text{ atm})(84.0 \text{ L})}{(0.0821 \frac{\text{atm}\cdot\text{L}}{\text{mol}\cdot\text{K}})(298.15 \text{ K})} = 3.431636791 \text{ mol} \\ \Delta H &= n\Delta H_{\text{rxn}} \quad \Delta H_{\text{rxn}} = \frac{\Delta H}{n} = \frac{116.2 \text{ kJ}}{3.431636791 \text{ mol}} \quad \Delta H_{\text{rxn}} = 33.9 \text{ kJ/mol} \\ \text{N}_2(g) + 2 \text{O}_2(g) &\rightarrow 2 \text{NO}_2(g) \quad \Delta H = 67.8 \text{ kJ} \quad (2 \text{ mol of NO}_2 \text{ in Eq}) \\ \text{or } \frac{1}{2} \text{N}_2(g) + \text{O}_2(g) &\rightarrow \text{NO}_2(g) \quad \Delta H = 33.9 \text{ kJ} \end{aligned}$$

Example 2: Given that $2 \text{C}_4\text{H}_{10}(g) + 13 \text{O}_2(g) \rightarrow 8 \text{CO}_2(g) + 10 \text{H}_2\text{O}(g) + 5317 \text{ kJ}$, calculate the change in enthalpy when 28.2 g of butane is burned.

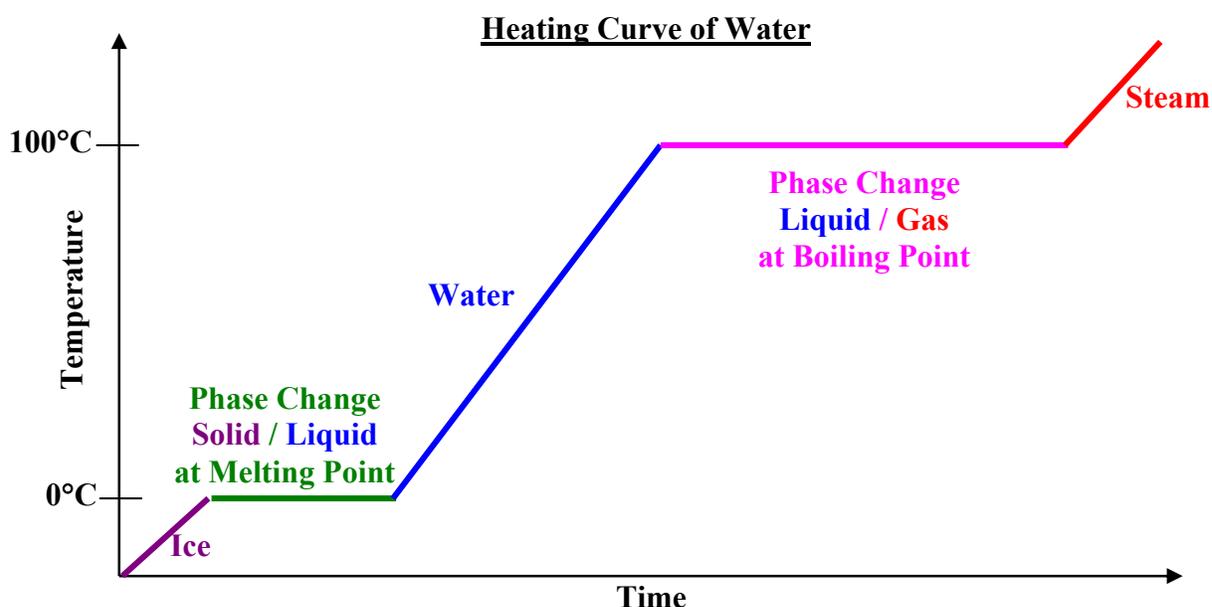
$$\begin{aligned} \Delta H_{\text{rxn}} &= \frac{-5317 \text{ kJ}}{2 \text{ mol}} = -2658.5 \text{ kJ/mol} && \text{(There are 2 moles of C}_4\text{H}_{10} \text{ in the chemical equation for 5317 kJ.)} \\ n &= \frac{28.2 \text{ g}}{58.14 \text{ g/mol}} = 0.4850361197 \text{ mol C}_4\text{H}_{10} && \Delta H = n\Delta H_{\text{rxn}} = (0.4850361197 \text{ mol})(-2658.5 \text{ kJ/mol}) \\ \Delta H &=? && \Delta H = -1.29 \times 10^3 \text{ kJ} = -1.29 \text{ MJ} \quad (1 \text{ MJ} = 1000 \text{ kJ}) \end{aligned}$$

Assignment**6.4 pg. 199 #21 to 28**

6.5 & 12.6: Calorimetry and Phase Changes**Energy involved in Physical Change (Temperature or Phase Change):**

Heating Curve: - a graph of temperature 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 acquired enough energy to overcome the intermolecular forces necessary. This is commonly referred to as the **potential change** of a substance.
- when a substance is undergoing **temperature change** within a particular phase, it is referred to as **kinetic change** (because temperature is also referred 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 enthalpies of fusion and vapourization.

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

Specific Heat (*s*): - 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

$$q = n\Delta H_{\text{fus}}$$

$$q = n\Delta H_{\text{vap}}$$

$$q = n\Delta H_{\text{sub}}$$

q = Heat Change (J or kJ)

n = moles

ΔH_{fus} = Molar Enthalpy of Fusion (kJ/mol)

ΔH_{vap} = Molar Enthalpy of Vaporization (kJ/mol)

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

Physical Kinetic Change

$$q = ms\Delta T$$

$$q = C\Delta T$$

$$C = ms$$

q = Heat Change (J or kJ) m = mass (g or kg) ΔT = Change in Temperature (in °C or K)

s = 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 [kJ/(kg • °C)]	ΔH_{fus} (kJ/mol)	ΔH_{vap} (kJ/mol)
Ice H ₂ O _(s)	0	----	2.03	6.01	----
Water H ₂ O _(l)	----	100	4.184	----	40.79
Steam H ₂ O _(g)	----	----	1.99	----	----
Ammonia NH _{3(g)}	-77.73	-33.34	2.06	5.66	23.33
Methanol CH ₃ OH _(l)	-98	64.6	2.53	3.22	35.21
Ethanol C ₂ H ₅ OH _(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 $q = n\Delta H_{\text{vap}}$.

$$\Delta H_{\text{vap}} = 40.79 \text{ kJ/mol}$$

$$n = \frac{36.04 \text{ g}}{18.02 \text{ g/mol}} = 2.000 \text{ mol H}_2\text{O}$$

$$q = ?$$

$$q = n\Delta H_{\text{vap}}$$

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

$$q = 81.58 \text{ kJ}$$

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 $q = mc\Delta T$.

$$s = 4.184 \text{ J/(g} \cdot \text{°C)}$$

$$m = 100.0 \text{ g H}_2\text{O}$$

$$\Delta T = 80.0^\circ\text{C} - 20.0^\circ\text{C} = 60.0^\circ\text{C}$$

$$q = ?$$

$$q = ms\Delta T$$

$$q = (100.0 \text{ g})(4.184 \text{ J/(g} \cdot \text{°C)})(60.0^\circ\text{C}) = 25104 \text{ J}$$

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

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

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

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

$$\Delta H_{\text{sub}} = 5.66 \text{ kJ/mol} + 23.33 \text{ kJ/mol}$$

$$\Delta H_{\text{sub}} = 28.99 \text{ kJ/mol}$$

$$n = \frac{40.0 \text{ g}}{17.04 \text{ g/mol}} = 2.34741784 \text{ mol NH}_3$$

$$q = ?$$

$$q = n\Delta H_{\text{sub}}$$

$$q = (2.34741784 \text{ mol})(28.99 \text{ kJ/mol})$$

$$q = 68.1 \text{ kJ}$$

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).

$$m = 18.02 \text{ g H}_2\text{O} = 0.01802 \text{ kg H}_2\text{O}$$

$$n = \frac{18.02 \text{ g}}{18.02 \text{ g/mol}} = 1.000 \text{ mol H}_2\text{O}$$

$$s_{\text{water}} = 4.184 \text{ kJ/(kg} \cdot \text{°C)}$$

$$\Delta T_{\text{water}} = 100.0^\circ\text{C} - 80.0^\circ\text{C} = 20.0^\circ\text{C}$$

$$\Delta H_{\text{vap}} = 40.79 \text{ kJ/mol}$$

$$s_{\text{steam}} = 1.99 \text{ kJ/(kg} \cdot \text{°C)}$$

$$\Delta T_{\text{steam}} = 115^\circ\text{C} - 100^\circ\text{C} = 15^\circ\text{C}$$

$$q_{\text{total}} = ?$$

$$q_{\text{total}} = ms_w\Delta T_w + n\Delta H_{\text{vap}} + ms_s\Delta T_s$$

(water) (vaporization) (steam)

$$q_{\text{total}} = (0.01802 \text{ kg})(4.184 \text{ kJ/(kg} \cdot \text{°C)})(20.0^\circ\text{C}) +$$

$$(1.000 \text{ mol})(40.79 \text{ kJ/mol}) +$$

$$(0.01802 \text{ kg})(1.99 \text{ kJ/(kg} \cdot \text{°C)})(15^\circ\text{C})$$

$$q_{\text{total}} = 1.5079136 \text{ kJ} + 40.79 \text{ kJ} + 0.537897 \text{ kJ}$$

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

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

$$\Delta H = n\Delta H_{\text{soln}}$$

$$\Delta H = \text{Change in Enthalpy} \quad n = \text{moles} \quad \Delta H_{\text{soln}} = \text{Molar Enthalpy of Solution (kJ/mol)}$$

Example 5: 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?

$$\Delta H_{\text{soln}} = +26.2 \text{ kJ/mol} \quad (\Delta H_{\text{soln}} > 0; \text{ endothermic}) \quad \Delta H = n\Delta H_{\text{soln}}$$

(Heat is absorbed from the surrounding) $\Delta H = (0.499625281 \text{ mol})(26.2 \text{ kJ/mol})$

$$n = \frac{40.0 \text{ g}}{80.06 \text{ g/mol}} = 0.499625281 \text{ mol NH}_4\text{NO}_3$$

$$\Delta H = 13.1 \text{ kJ absorbed}$$

$$\Delta H = ?$$

Example 6: 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 .

$$\Delta H_{\text{soln}} = -82.8 \text{ kJ/mol} \quad (\Delta H_{\text{soln}} < 0; \text{ exothermic}) \quad \Delta H = n\Delta H_{\text{soln}} \quad n = \frac{\Delta H}{\Delta H_{\text{soln}}} = \frac{-12.9 \text{ kJ}}{-82.8 \text{ kJ/mol}}$$

(Heat is released into the surrounding)

$$\Delta H = -12.9 \text{ kJ}$$

$$M = 110.98 \text{ g/mol CaCl}_2$$

$$n = 0.1557971014 \text{ mol}$$

$$n = ? \quad m = ?$$

$$m = nM = (0.1557971014 \text{ mol})(110.98 \text{ g/mol})$$

$$m = 17.3 \text{ g}$$

Heat of Dilution: - the amount of heat associated during the dilution process of a solution,

- a solution that has an endothermic heat of solution ($\Delta H_{\text{soln}} > 0$) will have an endothermic heat of dilution.
- a solution that has an exothermic heat of solution ($\Delta H_{\text{soln}} < 0$) will have an exothermic heat of dilution.

(**Examples:** When $\text{NaOH}_{(s)}$ is dissolved to become $\text{NaOH}_{(aq)}$, 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 $\text{H}_2\text{SO}_4_{(aq)}$ 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.**)

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 7: 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.

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

$$s = 4.184 \text{ J/(g} \cdot ^\circ\text{C)}$$

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

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

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

$$\text{Heat Lost} = \text{Heat Gained}$$

(hot water, kinetic) (cold water, kinetic)

$$m_{\text{hw}}s\Delta T_{\text{hw}} = m_{\text{cw}}s\Delta T_{\text{cw}}$$

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

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

Example 8: 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?

$T_f = ?$

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

$$s_{\text{Fe}} = 0.444 \text{ J}/(\text{g} \cdot ^\circ\text{C})$$

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

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

$$s_{\text{water}} = 4.184 \text{ J}/(\text{g} \cdot ^\circ\text{C})$$

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

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

$$m_{\text{Fe}}s_{\text{Fe}}\Delta T_{\text{Fe}} = m_{\text{w}}s_{\text{w}}\Delta T_{\text{w}}$$

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

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

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

$$-4850T_f = -324380$$

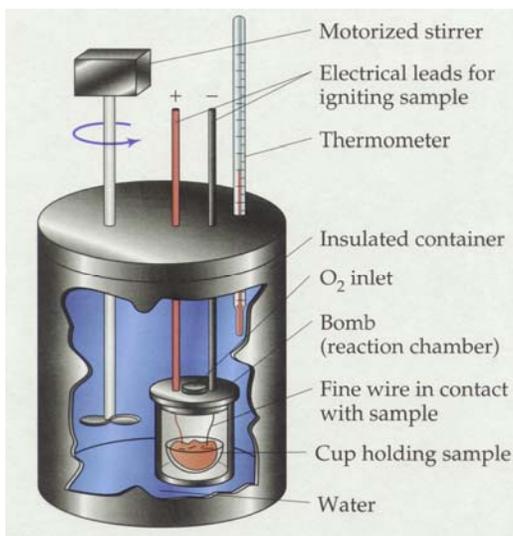
$$T_f = \frac{-324380}{-4850}$$

$$T_f = 66.9^\circ\text{C}$$

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 $\Delta H_{\text{comb}} < 0$.



Schematic of a Bomb Calorimeter

Enthalpy of Combustion

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

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 used 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)

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

or

$$n_{\text{sample}}\Delta H_{\text{comb}} = m_{\text{w}}s_{\text{w}}\Delta T \text{ (if the heat absorbed by the calorimeter itself is ignored)}$$

Example 9: 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

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

a. $m_{octane} = 32.65$ g
 $n_{octane} = \frac{32.65 \text{ g}}{114.26 \text{ g/mol}} = 0.2857517942$ mol C_8H_{18}

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

$\Delta H_{comb} = ?$

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

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

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

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

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

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

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

% 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

ΔH_{rxn} = Molar Heat of Reaction (kJ/mol)

ΔH_{ion} = Molar Heat of Ionization (kJ/mol)

n = moles

ΔH_{neut} = Molar Heat of Neutralization (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)

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

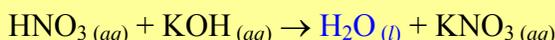
$$n_{\text{sample}}\Delta H_{\text{fus}} = m_w s_w \Delta T \quad (\text{physical change - molar heat of fusion})$$

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

$$m_{\text{sample}} s_{\text{sample}} \Delta T_{\text{sample}} = m_w s_w \Delta T_w \quad (\text{physical change - specific heat})$$

Example 10: When 250.0 mL of $\text{HNO}_3(aq)$ at 0.300 mol/L is reacted with 250.0 mL of $\text{KOH}(aq)$ 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 $\text{HNO}_3(aq)$ and $\text{KOH}(aq)$.

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



Assuming $\text{KNO}_3(aq)$ 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** ($0.300 \text{ mol/L} \times 0.2500 \text{ L} = 0.0750 \text{ mol}$), the ΔH_{neut} for HNO_3 would be the same as KOH .

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

$$m_w = 0.5000 \text{ kg} \quad (500.0 \text{ mL is produced})$$

$$s_w = 4.184 \text{ kJ}/(\text{kg} \cdot ^\circ\text{C})$$

$$\Delta T = 28.60^\circ\text{C} - 22.10^\circ\text{C}$$

$$\Delta T = 6.50^\circ\text{C}$$

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

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

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

$$\Delta H_{\text{neut}} = \frac{(0.5000 \text{ kg})(4.184 \text{ kJ}/(\text{kg} \cdot ^\circ\text{C}))(6.50^\circ\text{C})}{(0.0750 \text{ mol})}$$

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

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

Assignment

12.6 pg. 421–423 #69, 71, 72, 78, 112

6.5 pg. 199– 200 #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_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** .

($\text{H}_2\text{O}(g)$ has $\Delta H_f^\circ = -241.8 \text{ kJ/mol}$; $\text{H}_2\text{O}(l)$ has $\Delta H_f^\circ = -285.8 \text{ kJ/mol}$)

(See Appendix 2 on pg. A2 to A5 in the Chang 9th ed. Chemistry textbook for a list of ΔH_f°)

Standard Enthalpy of Formation (Chemical)

$$\Delta H = n\Delta H_f^\circ$$

ΔH = Change in Enthalpy n = moles ΔH_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.

$$\Delta H = -822 \text{ kJ}$$

$$n = 2 \text{ mol of NaCl}$$

$$\Delta H_f^\circ = ?$$

$$\Delta H = n\Delta H_f^\circ$$

$$\Delta H_f^\circ = \frac{\Delta H}{n} = \frac{-822 \text{ kJ}}{2 \text{ mol}}$$

$$\Delta H_f^\circ = -411 \text{ kJ/mol}$$

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

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

$$\Delta H_f^\circ = -393.5 \text{ kJ/mol}$$

$$\Delta H = ?$$

$$\Delta H = n\Delta H_f^\circ$$

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

$$\Delta H = -894 \text{ kJ} \quad (894 \text{ kJ is released})$$

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 ($\Delta H_f^\circ = -822.2 \text{ kJ/mol}$ for Fe_2O_3)?

$$\Delta H = -1.20 \text{ MJ} = -1.20 \times 10^3 \text{ kJ (exothermic)} \quad \Delta H = n\Delta H_f^\circ$$

$$\Delta H_f^\circ = -822.2 \text{ kJ/mol}$$

$$M = 159.7 \text{ g/mol Fe}_2\text{O}_3$$

$$n = ?$$

$$m = ?$$

$$n = \frac{\Delta H}{\Delta H_f^\circ} = \frac{-1.20 \times 10^3 \text{ kJ}}{-822.2 \text{ kJ/mol}} = 1.459498905 \text{ mol}$$

$$m = nM = (1.459498905 \text{ mol})(159.7 \text{ g/mol}) \quad m = 233 \text{ g}$$

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.

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

$$\Delta H = -12.2 \text{ kJ (exothermic)}$$

$$\Delta H_f^\circ = ?$$

$$\Delta H = n\Delta H_f^\circ$$

$$\Delta H_f^\circ = \frac{\Delta H}{n} = \frac{-12.2 \text{ kJ}}{0.3935444895 \text{ mol}}$$

$$\Delta H_f^\circ = -31.0 \text{ kJ/mol}$$

Standard Molar Enthalpy of Reaction (ΔH_{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.

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

- 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.

Direct Method to determine Standard Enthalpy of Reaction

$$\Delta H^{\circ}_{\text{rxn}} = \Sigma H^{\circ}_{\text{products}} - \Sigma H^{\circ}_{\text{reactants}}$$

$\Delta H^{\circ}_{\text{rxn}}$ = Change in Enthalpy of Reaction

$\Sigma H^{\circ}_{\text{products}}$ = Sum of Heat of Products (from all $n\Delta H^{\circ}_f$ of products)

$\Sigma H^{\circ}_{\text{reactants}}$ = Sum of Heat of Reactants (from all $n\Delta H^{\circ}_f$ of reactants)

Example 5: Propane is a clean burning fossil fuel that is widely used in outdoor barbecue.

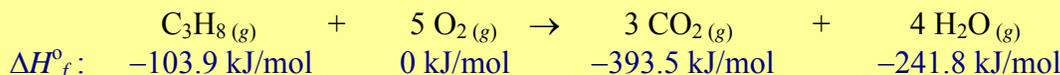
a. Calculate the standard molar enthalpy of combustion for propane.

$$(\Delta H^{\circ}_f \text{C}_3\text{H}_8 = -103.9 \text{ kJ/mol}; \Delta H^{\circ}_f \text{CO}_2 = -393.5 \text{ kJ/mol}; \Delta H^{\circ}_f \text{H}_2\text{O}_{(g)} = -241.8 \text{ kJ/mol})$$

b. Draw its potential energy diagram.

c. How much energy will be absorbed or released when 15.0 g of propane is burned?

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



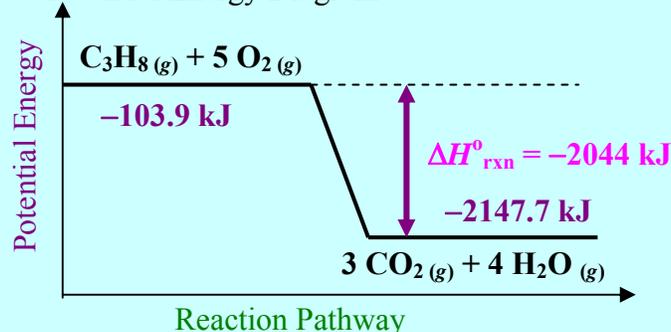
$$\Delta H^{\circ}_{\text{rxn}} = \Sigma H^{\circ}_{\text{products}} - \Sigma H^{\circ}_{\text{reactants}}$$

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

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

$$\Delta H^{\circ}_{\text{rxn}} = -2044 \text{ kJ/mol of C}_3\text{H}_8 \text{ burned}$$

b. Potential Energy Diagram



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

$$n = \frac{15.0 \text{ g}}{44.10 \text{ g/mol}} = 0.3401360544 \text{ mol C}_3\text{H}_8$$

$$\Delta H^{\circ}_{\text{rxn}} = -2043.8 \text{ kJ/mol} \quad \Delta H = ?$$

$$\Delta H = n\Delta H^{\circ}_{\text{rxn}}$$

$$\Delta H = (0.3401360544 \text{ mol})(-2043.8 \text{ kJ/mol})$$

$$\Delta H = -695 \text{ kJ} \quad (695 \text{ kJ is released})$$

Example 6: Find the amount of heat released when 34.9 g of butane gas is burned at standard conditions.

$$(\Delta H^{\circ}_f \text{C}_4\text{H}_{10} = -124.7 \text{ kJ/mol}; \Delta H^{\circ}_f \text{CO}_2 = -393.5 \text{ kJ/mol}; \Delta H^{\circ}_f \text{H}_2\text{O}_{(g)} = -241.8 \text{ kJ/mol})$$

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



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



$$\Delta H_f: \quad -124.7 \text{ kJ/mol} \quad 0 \text{ kJ/mol} \quad -393.5 \text{ kJ/mol} \quad -241.8 \text{ kJ/mol}$$

$$\Delta H^{\circ}_{\text{rxn}} = \Sigma H^{\circ}_{\text{products}} - \Sigma H^{\circ}_{\text{reactants}}$$

$$\Delta H^{\circ}_{\text{rxn}} = [4 \text{ mol} (-393.5 \text{ kJ/mol}) + 5 \text{ mol} (-241.8 \text{ kJ/mol})] - [1 \text{ mol} (-124.7 \text{ kJ/mol}) + \frac{13}{2} \text{ mol} (0 \text{ kJ/mol})]$$

$$\Delta H^{\circ}_{\text{rxn}} = [-2783 \text{ kJ}] - [-124.7 \text{ kJ}]$$

$$\Delta H_{\text{rxn}} = -2658.3 \text{ kJ/mol of C}_4\text{H}_{10} \text{ burned}$$

$$n = \frac{34.9 \text{ g}}{58.14 \text{ g/mol}} = 0.6002751978 \text{ mol C}_4\text{H}_{10}$$

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

$$\Delta H = (0.6002751978 \text{ mol})(-2658.3 \text{ kJ/mol}) = -1595.7 \text{ kJ}$$

$$\Delta H_{\text{rxn}} = -2658.3 \text{ kJ/mol} \quad \Delta H = ?$$

$$\Delta H = -1.60 \text{ MJ} \quad (1.60 \text{ MJ is released})$$

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,

- determine the experimental standard molar enthalpy of combustion heptane.
- find the theoretical standard molar enthalpy of combustion of heptane.
(ΔH_f° heptane = -224.2 kJ/mol)
- explain why the experimental ΔH_{rxn}° is different than its theoretical counterpart.

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

$$n = \frac{10.02 \text{ g}}{100.23 \text{ g/mol}}$$

$$n = 0.0999700688 \text{ mol C}_7\text{H}_{16}$$

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

$$\Delta T = 85.0^\circ\text{C} - 20.0^\circ\text{C} = 65.0^\circ\text{C}$$

$$s_{\text{water}} = 4.184 \text{ kJ / (kg} \cdot ^\circ\text{C)}$$

$$\Delta H_{rxn}^\circ = ?$$

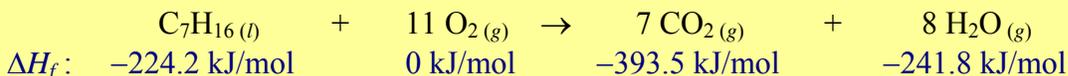
$$n\Delta H_{rxn}^\circ = m_w s_w \Delta T$$

$$\Delta H_{rxn}^\circ = \frac{m_w s_w \Delta T}{n} = \frac{(1.50 \text{ kg})(4.184 \text{ kJ/(kg} \cdot ^\circ\text{C)})(65.0^\circ\text{C})}{(0.0999700688 \text{ mol})}$$

$$\Delta H_{rxn}^\circ = 4080.621377 \text{ kJ/mol (released)}$$

$$\text{Experimental } \Delta H_{rxn}^\circ = -4.08 \text{ MJ/mol of C}_7\text{H}_{16} \text{ burned}$$

b. To find theoretical ΔH_{rxn}° for the combustion of heptane, we have to use the direct method.



$$\Delta H_{rxn}^\circ = \Sigma H_{\text{products}}^\circ - \Sigma H_{\text{reactants}}^\circ$$

$$\Delta H_{rxn}^\circ = [7 \text{ mol}(-393.5 \text{ kJ/mol}) + 8 \text{ mol}(-241.8 \text{ kJ/mol})] - [1 \text{ mol}(-224.8 \text{ kJ/mol})]$$

$$\Delta H_{rxn}^\circ = [-4688.9 \text{ kJ}] - [-224.8 \text{ kJ}] = -4464.1 \text{ kJ}$$

$$\text{Theoretical } \Delta H_{rxn}^\circ = -4.46 \text{ MJ/mol of C}_7\text{H}_{16} \text{ burned}$$

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 H₂O_(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

- Determine the experimental molar enthalpy of formation of HCOOH_(l) assuming standard conditions. ($\Delta H_f^\circ \text{CO}_2 = -393.5 \text{ kJ/mol}$; $\Delta H_f^\circ \text{H}_2\text{O}_{(l)} = -285.8 \text{ kJ/mol}$)
- 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} .

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

$$n = 0.2003041495 \text{ mol HCOOH}$$

$$C_{\text{cal}} = 3.20 \text{ kJ/}^\circ\text{C}$$

$$\Delta T = 37.3^\circ\text{C} - 21.5^\circ\text{C} = 15.8^\circ\text{C}$$

$$\Delta H_{\text{rxn}}^\circ = ?$$

$$n\Delta H_{\text{rxn}}^\circ = C_{\text{cal}}\Delta T$$

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

$$\Delta H_{\text{rxn}}^\circ = 252.4161388 \text{ kJ/mol (released)}$$

Experimental $\Delta H_{\text{rxn}}^\circ = -252 \text{ kJ/mol}$ of HCOOH burned

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



$$\Delta H_{\text{rxn}}^\circ = \Sigma H_{\text{products}}^\circ - \Sigma H_{\text{reactants}}^\circ$$

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

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

$$\Delta H_f^\circ = -679.3 \text{ kJ} + 252.4161388 \text{ kJ} = -426.8838612 \text{ kJ}$$

Experimental ΔH_f° of HCOOH = -427 kJ/mol

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

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

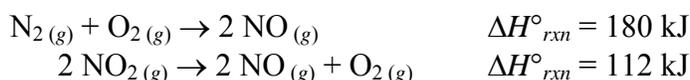
% error = 17.6%

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.

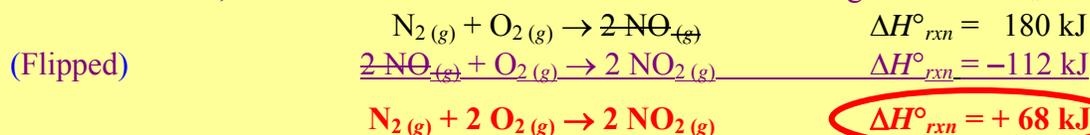
- when adding reactions, **compare the reactants and products of the overall net reaction with the intermediate (step) reactions given. Decide on the intermediate reactions that need to be reversed and / or multiply by a coefficient, such that when added, the intermediate products will cancel out perfectly 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>)

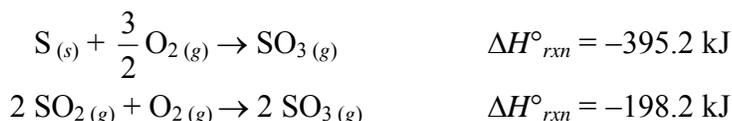
Example 9: Calculate ΔH°_{rxn} for the reaction $N_2(g) + 2 O_2(g) \rightarrow 2 NO_2(g)$, when the following reactions are given.



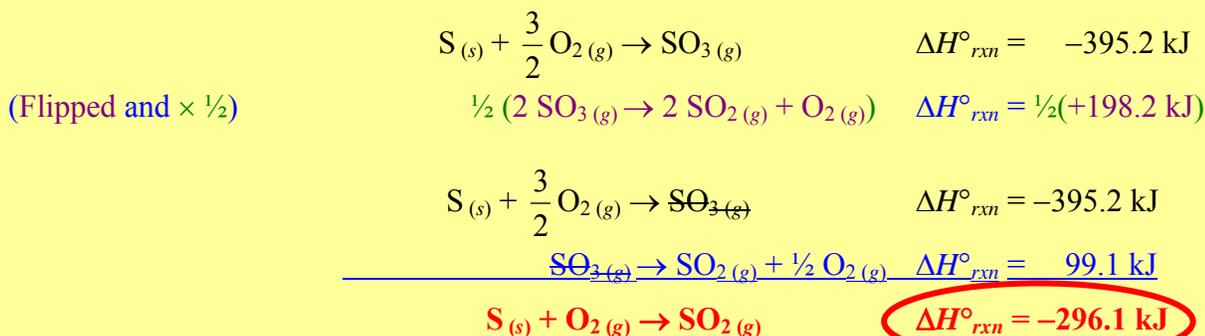
Note that 2 NO_2 in the net reaction is on the product side, whereas 2 NO_2 in the second reaction is on the reactant side. Hence, we need to reverse the second reaction and its sign of the ΔH°_{rxn} .



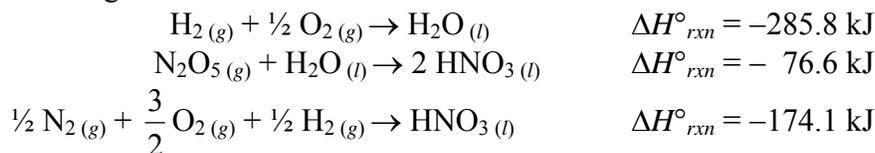
Example 10: Determine the ΔH°_{rxn} for the reaction $S(s) + O_2(g) \rightarrow SO_2(g)$, when the following reactions are given.



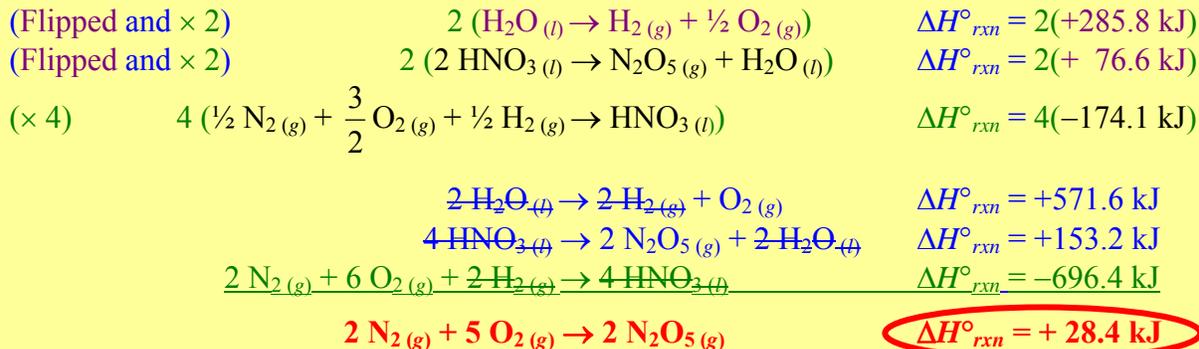
- SO_2 in the net reaction is on the product side, whereas 2 SO_2 in the second reaction is on the reactant side. Hence, we need to reverse the second reaction and its sign of the ΔH°_{rxn} .
- There is only 1 SO_2 in the net reaction, whereas there are 2 SO_2 in the second reaction. Therefore the second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



Example 3: Find the ΔH°_{rxn} for the overall reaction of $2 \text{N}_2(\text{g}) + 5 \text{O}_2(\text{g}) \rightarrow 2 \text{N}_2\text{O}_5(\text{g})$, when the following reactions are given.



- $2 \text{N}_2\text{O}_5$ 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} .
- There are $2 \text{N}_2\text{O}_5$ in the net reaction, whereas there is only $1 \text{N}_2\text{O}_5$ in the second reaction. Therefore the second reaction and its ΔH°_{rxn} need to be multiply by the coefficient of 2.
- There are 2N_2 in the next reaction on the reactant side. Since $\frac{1}{2} \text{N}_2$ 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.
- 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.



Assignment

6.6 pg. 200–202 #39 to 42, 45 to 49, 51, 52, 54 to 56, 58, 60 to 64, 67, 68, 74, 76, 80, 81

6.7: Present Sources of Energy and New Energy Sources

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

- 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.

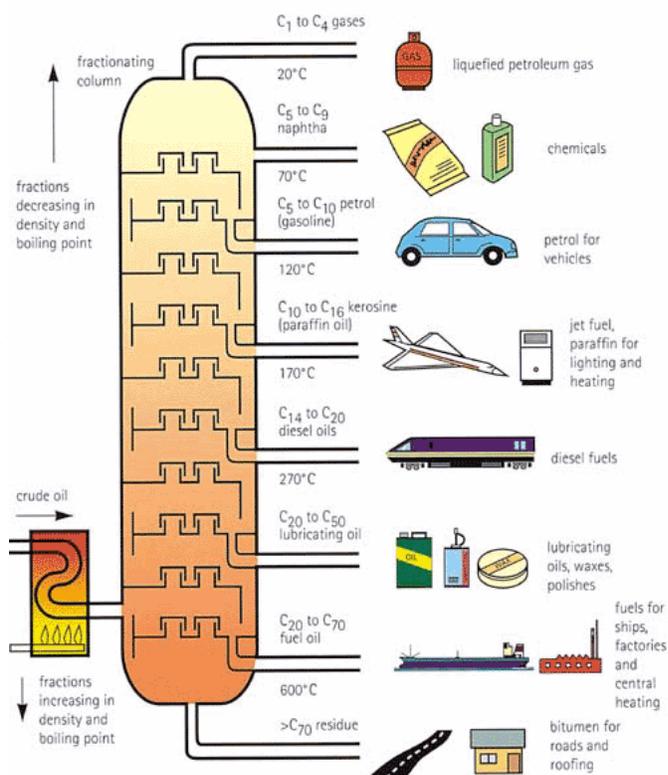
Example: Propane burns completely. $\text{C}_3\text{H}_8(\text{g}) + 5 \text{O}_2(\text{g}) \rightarrow 3 \text{CO}_2(\text{g}) + 4 \text{H}_2\text{O}(\text{g})$

- 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.

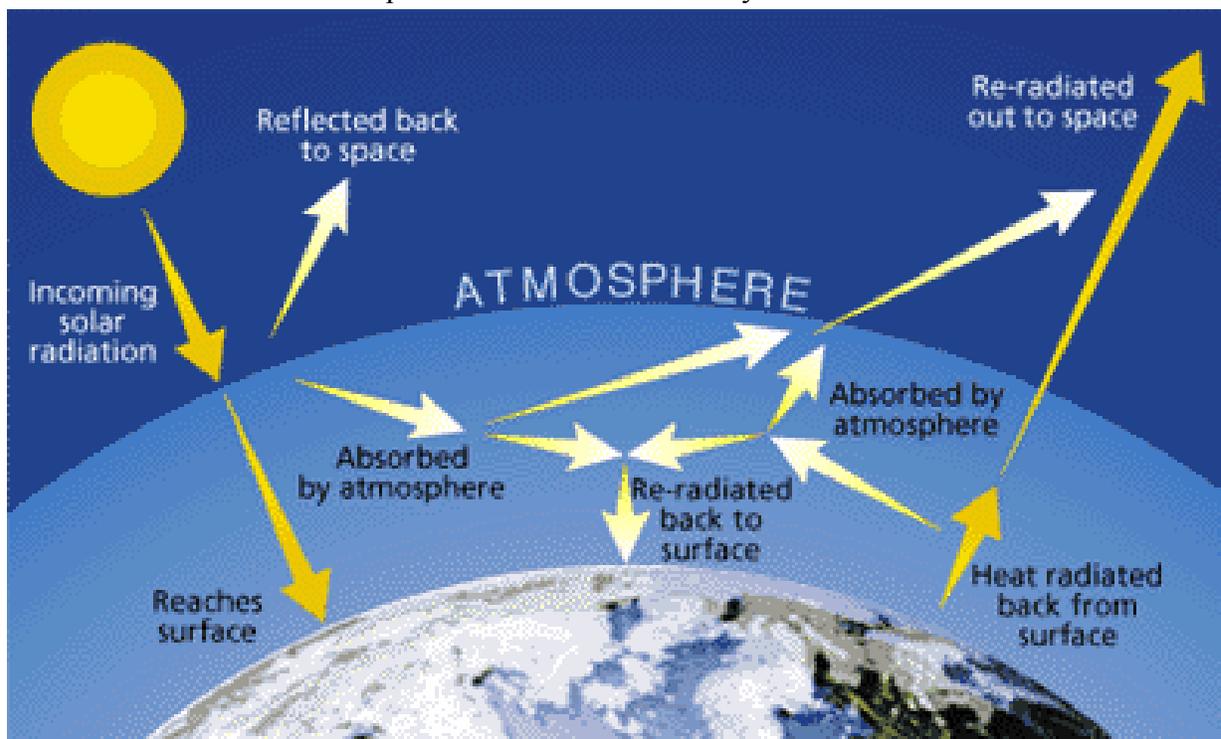
- Cracking:** - a chemical process whereby bigger alkanes are broken up into smaller ones using a catalyst and heat.
- since gasoline and natural gas only consists of 50% of crude oil, cracking is necessary to convert heavier fuel to more common fuel used in today's world.

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 greenhouse 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 (SF₆)** 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 CO₂ 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 CO₂ 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.

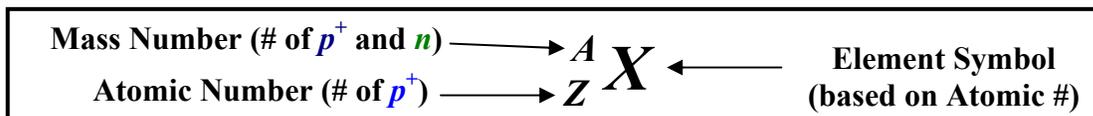
6. **Hydrogen Fuel**: - burning hydrogen to form water and generate heat and electricity.
 - very efficient and zero pollution.
 - hydrogen is very explosive and technologies are still needed for supplying and storing hydrogen safely in automobiles and homes.

Chapter 21: Nuclear Chemistry**21.1: The Nature of Nuclear Reactions**

Nucleons: - the particles that make up a nucleus of an atom (**protons**, (${}^1_1p^+$ or 1_1H) and **neutrons**, (1_0n)).

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



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.

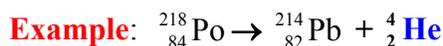
Nuclear Transmutation: - a process where radioactivity is resulted from the bombardment of nuclei by neutrons, protons or other nuclei.
- in most cases, heavier elements are synthesized from lighter elements.

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

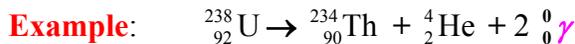
1. **Alpha Particle (α particle):** - basically a helium nucleus (4_2He), commonly found during radioactive decay from heavier nuclide (the net result is to **increase the neutron to proton ratio** – more explanation in the next section).



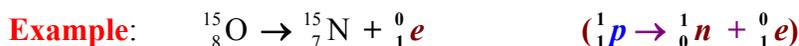
2. **Beta Particle (β particle):** - basically an electron (${}^0_{-1}e$ or ${}^0_{-1}\beta$) that is emitted when the neutron to proton ratio is higher than the zone of stability (**a neutron is transformed to a proton and an electron as a result** – more explanation in the next section).
- electrons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



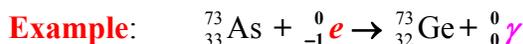
3. **Gamma Ray (γ ray)**: - also known as a high-energy photon (${}^0_0\gamma$) that is usually a by-product of an alpha-particle decay.
 - photon has no mass and no atomic number.



4. **Positron (e^+)**: - an antimatter of electron (0_1e 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**).



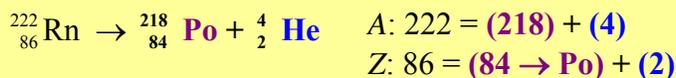
5. **Electron Capture**: - an inner-orbital electron is “captured” by the nucleus to **increase neutron to proton ratio**. It is usually accompanied by an emission of gamma ray.



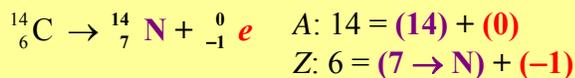
Balancing Nuclear Equations: - the total atomic number (Z) and the total atomic mass (A) have to balance on both sides.

Example 1: Balance the following nuclear equations.

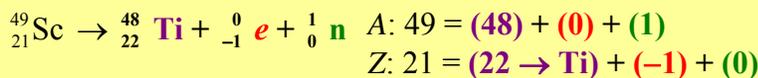
- a. ${}^{222}_{86}\text{Rn}$ produces an α particle.



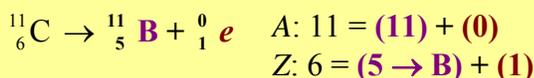
- b. ${}^{14}_6\text{C}$ produces a β particle.



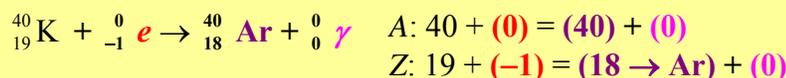
- c. ${}^{49}_{21}\text{Sc}$ produces a β particle and a neutron.



- d. ${}^{11}_6\text{C}$ produces a positron.



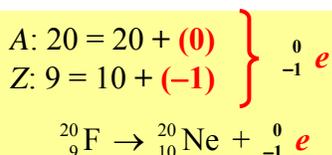
- e. ${}^{40}_{19}\text{K}$ captures an electron to produce γ ray



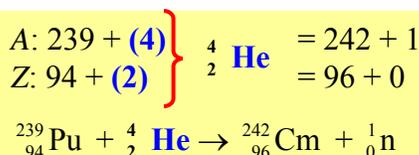
- f. ${}^1_1\text{H}$ reacts with ${}^{15}_7\text{N}$ to produce an α particle with γ ray.



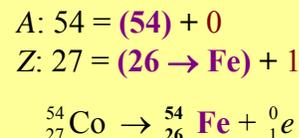
- g. ${}^{20}_9\text{F} \rightarrow {}^{20}_{10}\text{Ne} + \underline{\hspace{2cm}}$



- h. ${}^{239}_{94}\text{Pu} + \underline{\hspace{2cm}} \rightarrow {}^{242}_{96}\text{Cm} + {}^1_0n$



- i. ${}^{54}_{27}\text{Co} \rightarrow \underline{\hspace{2cm}} + {}^0_1e$

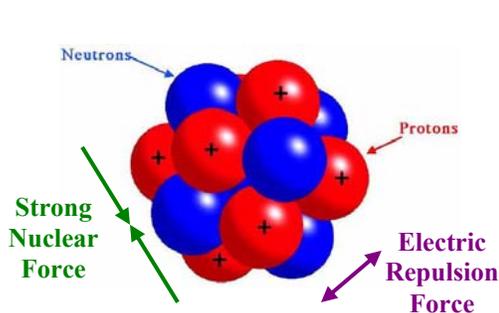


21.2: Nuclear Stability

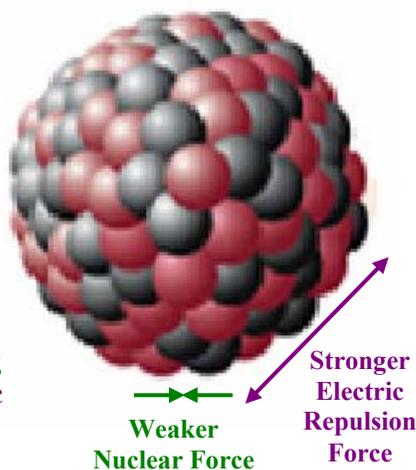
Strong Nuclear Force: - a force of attraction that is present over extremely short distance (1×10^{-15} m) between all nucleons (protons and neutrons).
 - it is much stronger than electromagnetic force in short distances. However, electromagnetic force is more significant over longer distances.

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**.



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).

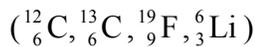
Radioactive Decay: - when a heavier nucleus loses nucleons to become a smaller but more stable nucleus. In the process, it gives off radiation products like alpha-, beta- particles and/or gamma rays.

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

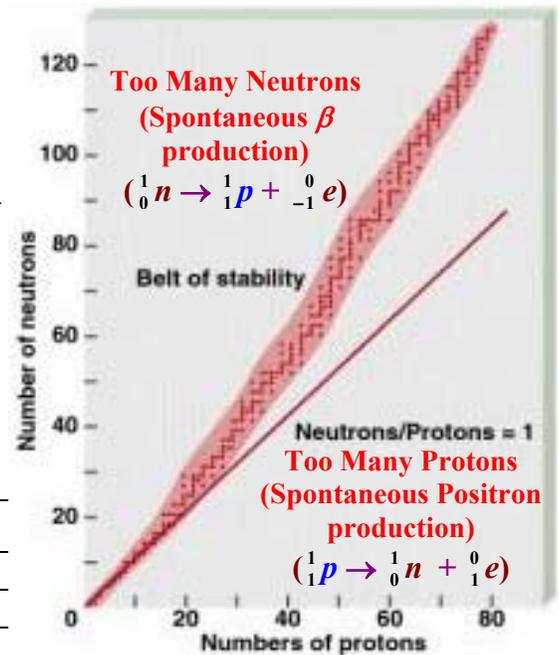
1. When a nuclide has 84 or more protons ($Z \geq 84$), it tends to be **unstable** and likely undergo **radioactive decay**.
2. Lighter nuclides are stable when $Z = n$ (or $n : p^+$ ratio = 1). However, heavier nuclides are stable only when $Z < n$ (or $n : p^+$ ratio > 1).
3. Nuclides with **even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



Nuclide	${}^{12}_6\text{C}$	${}^{13}_6\text{C}$	${}^{19}_9\text{F}$	${}^6_3\text{Li}$
# of p^+	6 (even)	6 (even)	9 (odd)	3 (odd)
# of n	6 (even)	7 (odd)	10 (even)	3 (odd)

Stability: Most \longrightarrow 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. ($\Delta m = m_{\text{products}} - m_{\text{reactants}}$)
 - 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).

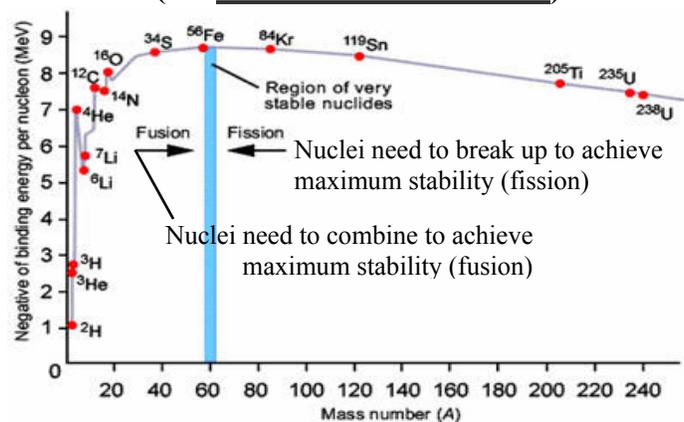
Subatomic Particle	Mass (kg)	Atomic Mass Unit (amu)
Neutron	1.67497×10^{-27}	1.008665
Proton	1.67357×10^{-27}	1.007825

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 ${}^{26}\text{Fe}$**).

Einstein's Mass-Energy Conversion

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

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.

$$m \text{ of } {}^{13}_6\text{C} = 13.003355 \text{ amu}$$

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

$$\Delta m = m \text{ of } {}^{13}_6\text{C} - m \text{ of } (6p^+ \text{ and } 7n) = 13.003355 \text{ amu} - 13.107605 \text{ amu} \quad \Delta m = -0.104250 \text{ amu}$$

$$\Delta E = -\Delta mc^2 = -(-0.104250 \text{ amu}) \left(\frac{1 \text{ kg}}{6.022 \times 10^{26} \text{ amu}} \right) (3.00 \times 10^8 \text{ m/s})^2 = 1.5580372 \times 10^{-11} \text{ J}$$

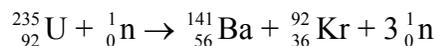
$$\Delta E_{\text{bind per nucleon}} = \frac{1.5580372 \times 10^{-11} \text{ J}}{13 \text{ nucleons}}$$

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

$$\Delta E_{\text{bind}} = 1.20 \times 10^{-12} \text{ J/nucleon} \times \frac{1 \text{ MeV}}{1.69 \times 10^{-13} \text{ J}}$$

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

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



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

$$m_{\text{initial}} \text{ of } {}^{235}_{92}\text{U} + {}^1_0\text{n} = 235.0439 \text{ amu} + 1.00899 \text{ amu} = 236.05289 \text{ amu}$$

$$m_{\text{final}} \text{ of } {}^{141}_{56}\text{Ba} + {}^{92}_{36}\text{Kr} + 3 {}^1_0\text{n} = 140.9144 \text{ amu} + 91.9262 \text{ amu} + 3(1.00899 \text{ amu}) = 235.86757 \text{ amu}$$

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

$$\Delta E = -\Delta mc^2 = -(-0.18532 \text{ amu}) \left(\frac{1 \text{ kg}}{6.022 \times 10^{26} \text{ amu}} \right) (3.00 \times 10^8 \text{ m/s})^2 = 2.76964464 \times 10^{-11} \text{ J/nucleus}$$

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

$$\Delta E_{\text{bind}} = 1.67 \times 10^{10} \text{ kJ/mol} = 16.7 \text{ TJ/mol}$$

$$1 \text{ TJ (Tera-Joules)} = 1 \times 10^{12} \text{ J}$$

Assignment

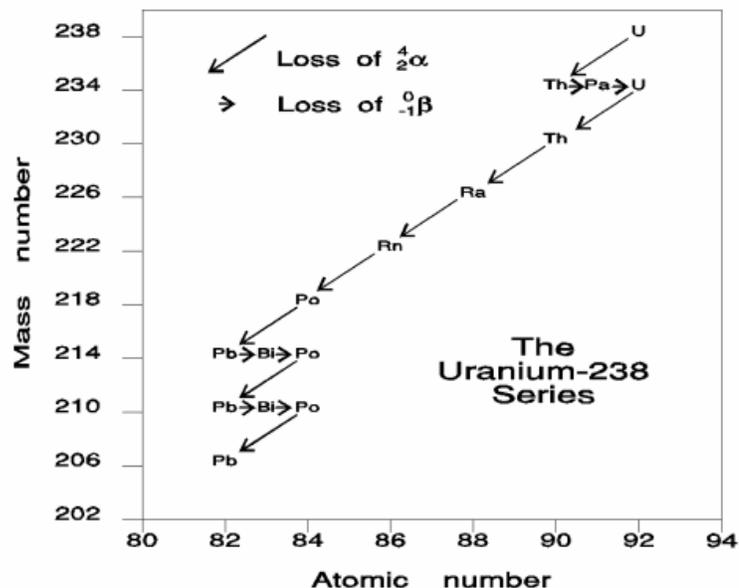
21.1 pg. 734 #1 to 6, pg. 736 #55

21.2 pg. 734–735 #7, 8, 11, 12, 14, 16, 18 to 20

21.3: 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:

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

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

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

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

Derivation Using Calculus:

$$\text{Rate} = -\frac{\Delta N}{\Delta t} = kN$$

$$\frac{1}{N} \Delta N = -k \Delta t$$

$$\int_{N_0}^N \frac{1}{N} dN = -k \int_0^t dt$$

$$\ln N - \ln N_0 = -kt$$

(k = Rate Constant,
 N = Amount of Nuclide)

(Rearrange for Integration,
 $\Delta N = dN$; $\Delta t = dt$)

(Integrate Both Sides: $\int \frac{1}{x} dx = \ln x$)

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

$$\ln\left(\frac{N}{N_0}\right) = -kt \quad (\text{Radioactive Decay Equation})$$

Half-Life ($t_{1/2}$): - the amount of time it takes to half the amount of radioactive nuclides.

- at **half-life, $t_{1/2}$** , the amount of radioactive nuclides $\frac{1}{2} N_0 = N$:

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

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

Radioactive Decay Equations

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

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

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

N = Amount of Nuclide at time t

k = Rate Constant (s^{-1} , min^{-1} , hr^{-1} , day^{-1} , yr^{-1})

N_0 = Amount of Nuclide at time 0

t = total decay time $t_{1/2}$ = 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 $^{99}_{43}\text{Tc}$ decays over time. What is the radioactive amount of $^{99}_{43}\text{Tc}$ after 2.00 days?

$N_0 = 100 \text{ mg}$
 $t_{1/2} = 6.0 \text{ hrs}$
 $t = 2.00 \text{ days} = 48.0 \text{ hrs}$
 $N = ?$

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

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

$$N = 0.391 \text{ mg}$$

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

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

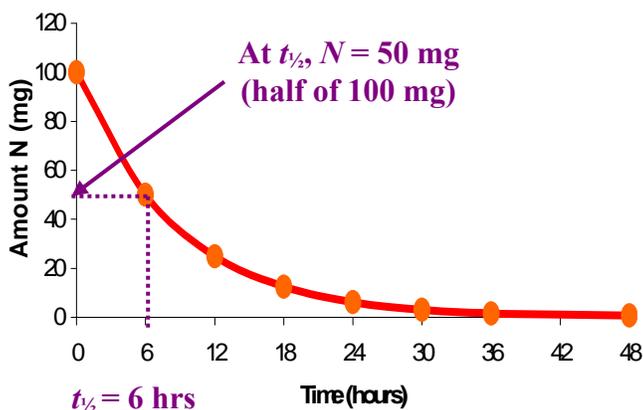
$$\ln\left(\frac{N}{N_0}\right) = -kt \quad \frac{N}{N_0} = e^{-kt}$$

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

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

$$N = 0.391 \text{ mg}$$

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.

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

$$t_{1/2} = 8.1 \text{ days}$$

$$\frac{N}{N_0} = 0.01$$

$$k = ?$$

$$t = ?$$

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

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

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

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

$$t = 54 \text{ days}$$

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

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

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

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

$$t = 54 \text{ days}$$

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.

$$N_0 = 50.0 \text{ mg}$$

$$N = 45.7 \text{ mg}$$

$$t = 24.0 \text{ hrs}$$

$$t_{1/2} = ?$$

$$k = ?$$

Solving k first:

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

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

$$k = 0.00375 \text{ hr}^{-1}$$

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

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

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

Solving $t_{1/2}$ first:

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

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

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

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

Then solve for k :

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

$$k = 0.00375 \text{ hr}^{-1}$$

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 ($^{14}_6\text{C} \rightarrow ^0_{-1}\text{e} + ^{14}_7\text{N}$).
 - 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 $^{14}_6\text{C}$ 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.

$$\frac{\text{Final Rate at } t}{\text{Initial Rate at } t=0} = \frac{kN}{kN_0} = \frac{5.2 \text{ counts}/(\text{min} \cdot \text{g})}{13.6 \text{ counts}/(\text{min} \cdot \text{g})} \quad t_{1/2} = 5730 \text{ yrs} \quad t = ?$$

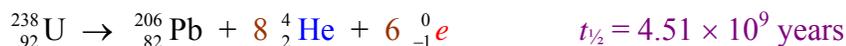
First, we solve for k .

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

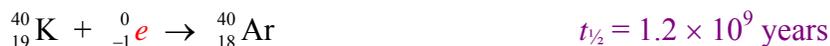
Next, we solve for t .

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

Uranium-238 Dating: - due to its lengthy half-life (4.51×10^9 years), it is used to date rocks and other ancient inorganic material. $^{238}_{92}\text{U}/^{206}_{82}\text{Pb}$ ratio is used as $^{238}_{92}\text{U}$ eventually decays to stable $^{206}_{82}\text{Pb}$.



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



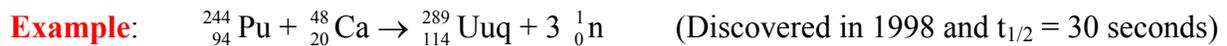
Assignment

21.3 pg. 735 #21, 23 to 26, 28, 29; pg. 737 #66 to 68, 85

21.4: Nuclear Transmutation

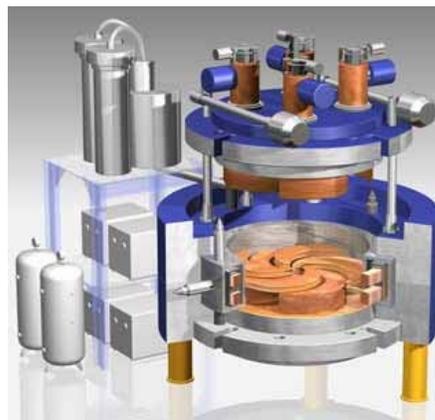
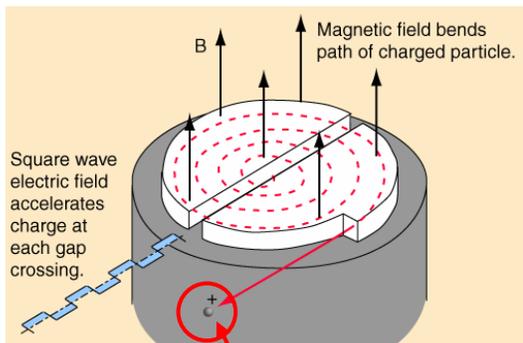
Nuclear Transmutation: - the reaction where one element is converted to another element by changing the number of protons.

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



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

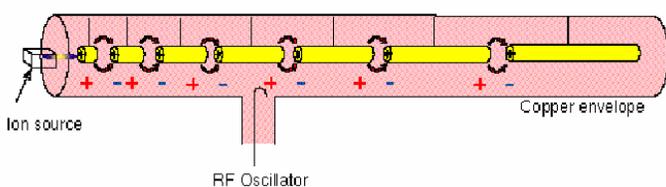
a. Cyclotron: - a type of particle accelerator that utilizes a changing electric field along with a magnetic field to increase the speed of an ion around a disc before hitting a target nuclide.



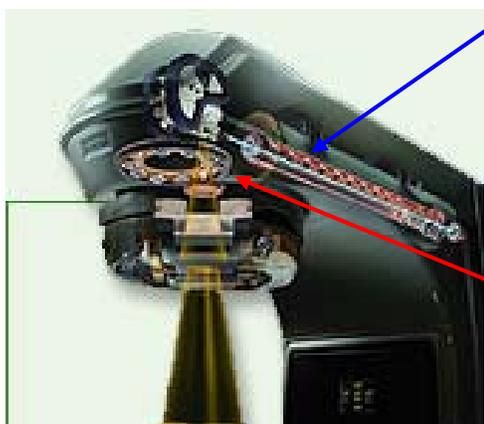
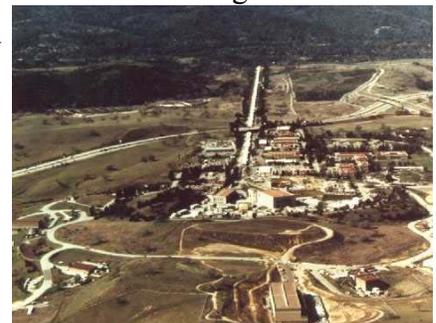
COMET: A medical superconducting cyclotron. It is used to generate thallium-201 (coronary arteries) and gallium-67 (soft-tissue tumors). It can also produce radio-pharmaceutical needed for PET and SPECT scans

Schematic of Accelerated charged particle to collide with target nuclide a Cyclotron

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.



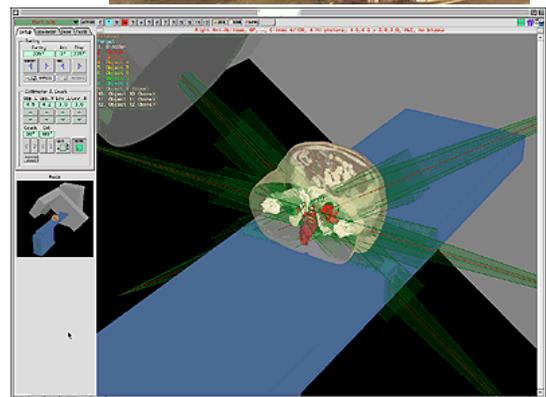
Left: Schematic of a Linear Accelerator
Right: Stanford Linear Accelerator



Linear Accelerator

Multileaf Collimeter to shape the beam

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

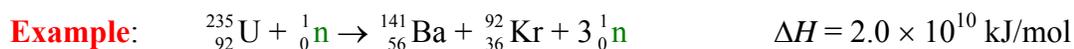


Schematic of a Medical Linear Accelerator

Assignment
21.4 pg. 735 #33 to 36

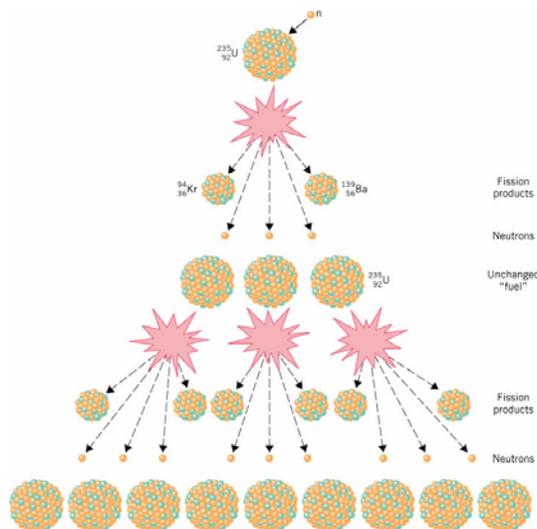
21.5: Nuclear Fission

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



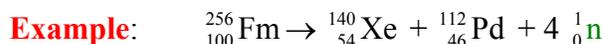
Chain Reaction: - when the nuclear fission is self-sustaining.

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



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 ($6 \times 10^{10} \text{ kJ} \approx 750 \text{ g of U-235}$) 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 ($8 \times 10^{10} \text{ kJ} \approx 1 \text{ kg of Pu-239}$) 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



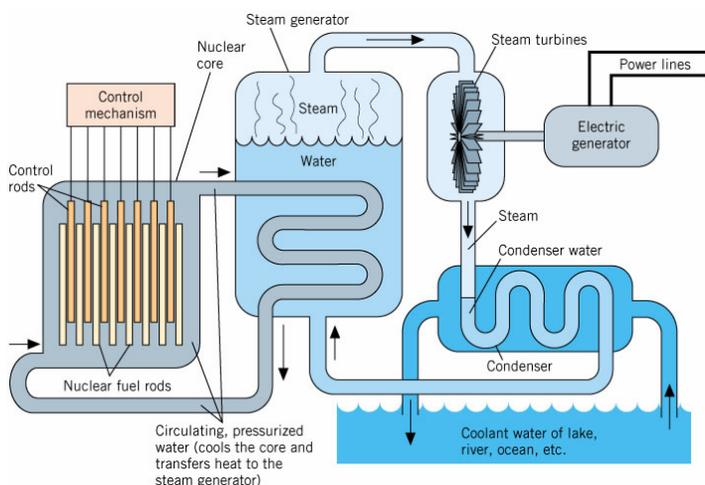
Plutonium Implosion Atomic Bomb (Fat Man)

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 $^{235}_{92}\text{U}$ 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 $^{235}_{92}\text{U}$ 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

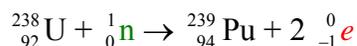
Light Water Reactor: - uses light water (regular H_2O) as moderator.

- 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 - $^2_1\text{H}_2\text{O}$) as moderator.

- D_2O does 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 $^{235}_{92}\text{U}$, 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.



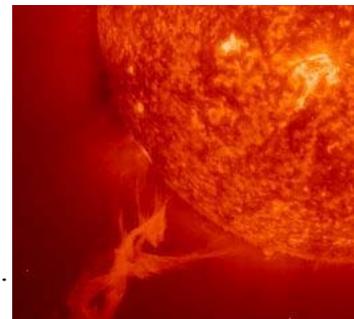
- it is the most expensive type of reactor due to its technical aspects. Currently, only Russia and France have a handful of breeder reactors.

21.6: Nuclear Fusion

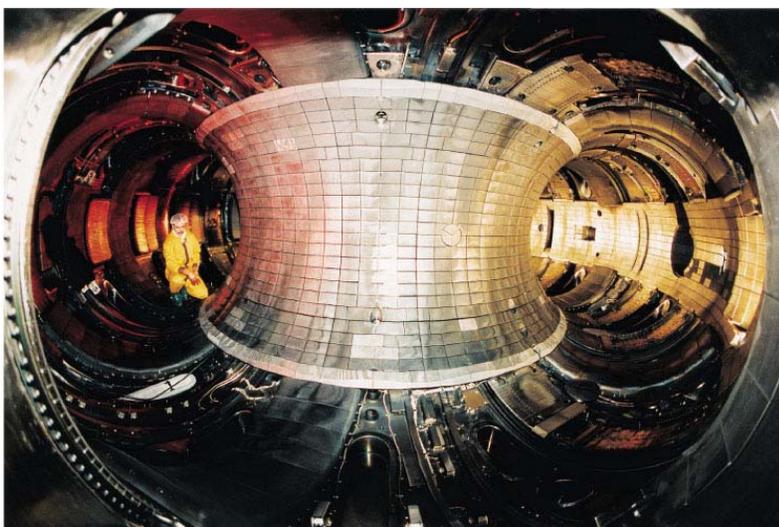
Nuclear Fusion: - the combining of two light nuclei into a heavier and more stable nucleus.



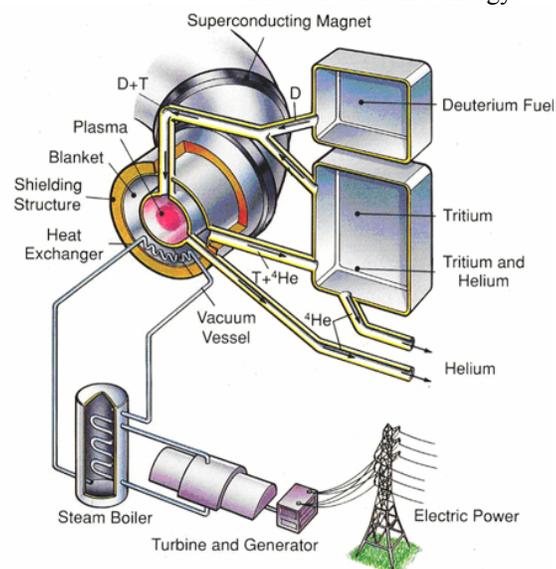
- the availability of hydrogen isotopes, deuterium (${}^2_1\text{H}$) and tritium (${}^3_1\text{H}$), in sea water and the harmless product, ${}^4_2\text{He}$, makes nuclear fusion an environmental friendly alternative to generate power.
- however, fusion reactions such as the one above usually require an initial temperature above $4 \times 10^7 \text{ K}$ 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.



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



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.

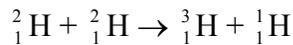


Propose Schematic of a Fusion Reactor to Generate Electricity

ITER'S TOKAMAK — TOO HOT TO HANDLE
 Fusion scientists often describe the job of containing a hot plasma in magnetic fields as akin to holding jelly using rubber bands.

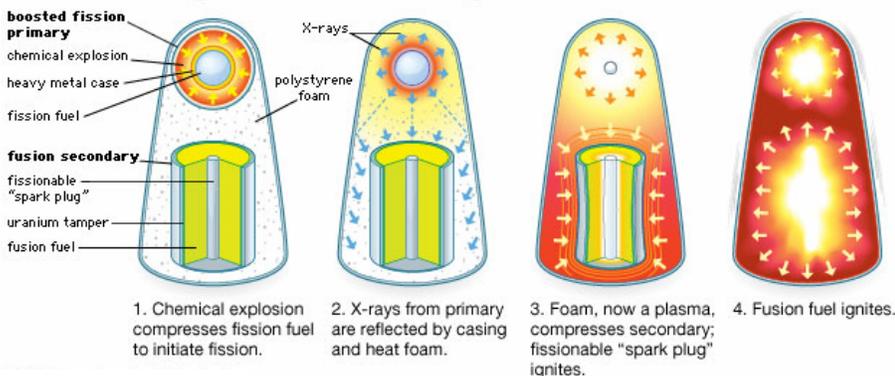
- Coils for magnetic field** • These superconducting magnets run both laterally and longitudinally around the machine. They are the 'rubber bands' that suspend the plasma in ITER's core.
- External heating** • In addition to the solenoid, ITER will use external radio waves and microwaves to heat the plasma to more than 100 million degrees centigrade.
- Divertor** • The divertor absorbs hot helium atoms from the fusion reaction. It must be able to withstand extreme temperatures and high levels of radiation.
- Solenoid** • A superconducting coil at the centre of the machine, the solenoid helps to stabilize the plasma and heats it through induction.
- Blanket** • The blanket surrounding the plasma absorbs neutrons and heat from the fusion reaction. It must be made of materials that can withstand high levels of radiation.
- Plasma** • Most likely consisting of deuterium and tritium, the plasma suspended within the reactor will release up to ten times the amount of energy it absorbs.

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_1H) which can be packed tightly. The detonations involve a fission reaction to generate the initial heat to start the fusion reaction.



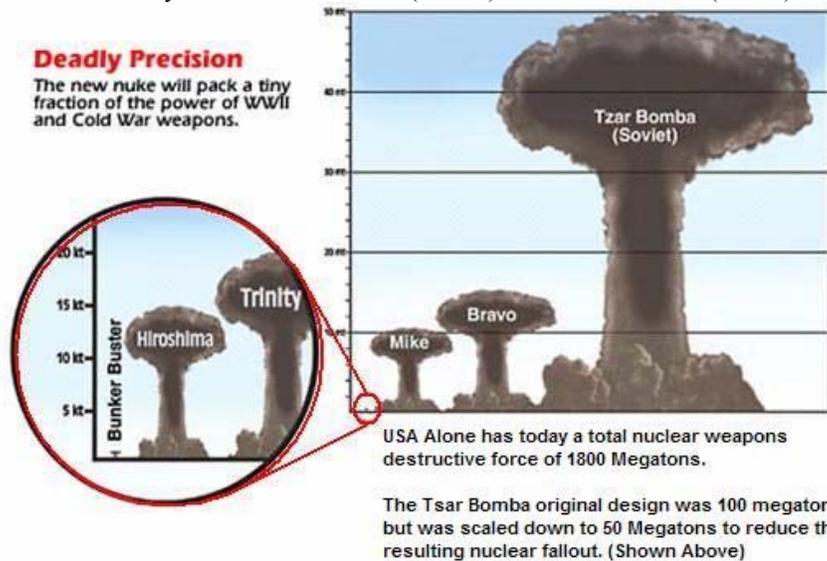
- fusion reaction is not limited by a critical mass as in fission reaction. Hence, the size of the explosion depends on the amount of fusion material.
- besides the intense heat to incinerate a large area, the damaging radiation effects come from the products of the fission starter and the product of 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.

Teller-Ulam two-stage thermonuclear bomb design



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, 1961 at Novaya Zemlya Island, (north of the Russia)

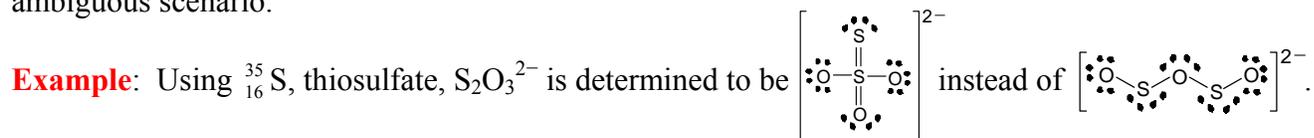
See Tsar Bomba explosion:
<http://www.youtube.com/watch?v=FfoQsZa8F1c> and
<http://www.youtube.com/watch?v=BmQIkDkZ7sk>

Assignment
 21.5 pg. 735–736 #38, 40, 41
 21.6 pg. 736 #44 to 46



21.7 & 21.8: 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.



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.

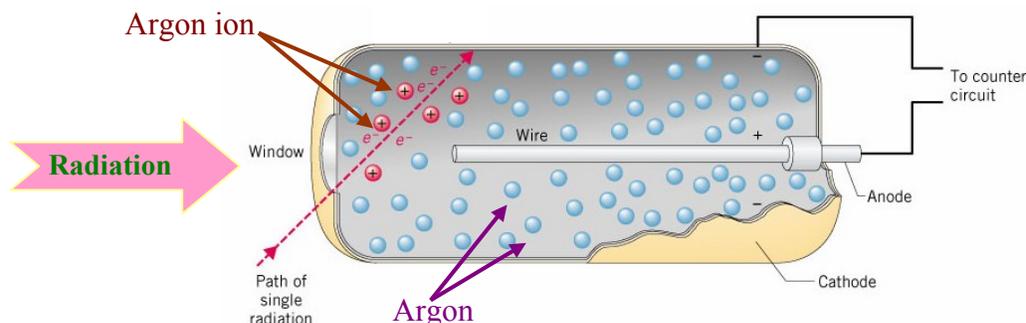
2. **Study of Photosynthesis**: - radioactive tracers like ^{14}C and ^{18}O can be included in determine the path of carbon and oxygen during the process of photosynthesis and other nutrient uptakes
3. **Isotopes in Medicine**: - compound that contain a radioactive tracer (**carrier compound**), can 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:

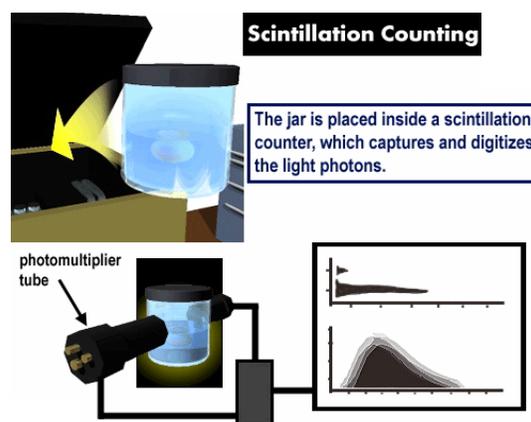
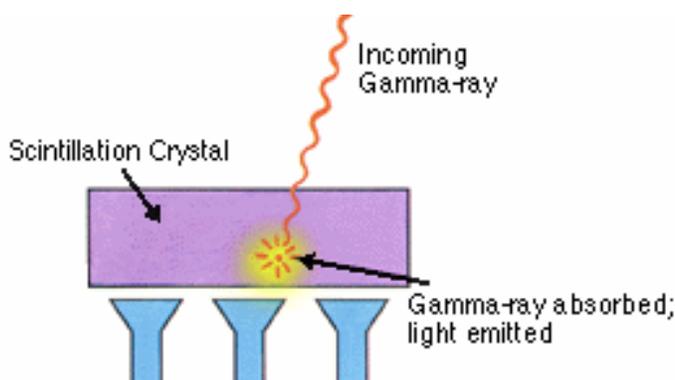
Radiotracers	Area of the Body Examine / Treatment	Other Usages
$^{131}_{53}\text{I}$	Thyroid	
$^{59}_{26}\text{Fe}$ and $^{51}_{24}\text{Cr}$	Red Blood Cells, Metabolism	Metallic Welds, Corrosion Mechanisms, Engine Wears
$^{252}_{98}\text{Cf}$	Cervical and Brain Cancer Treatments	Detections of Metal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

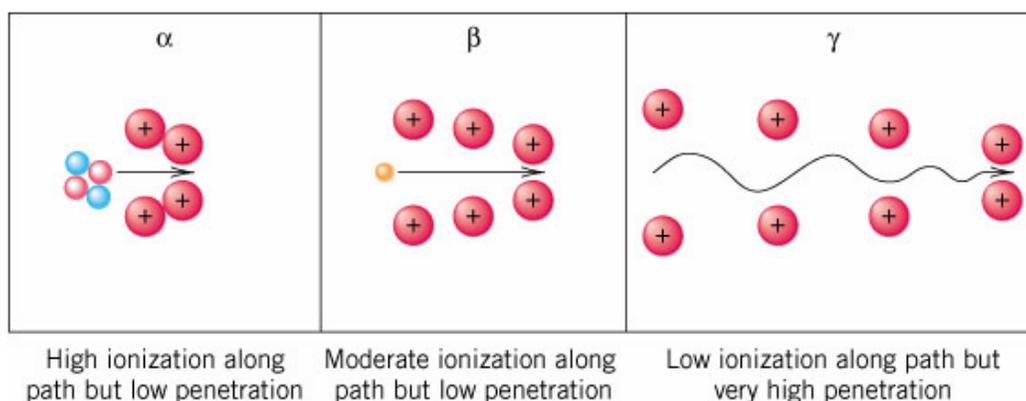
Examples: Genetic and DNA mutations

Sources of Radiation:

- 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 radon-222 (inert gas from natural uranium deposits); easily inhaled from basement cracks. Radon-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.
- 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 Fallout** can travel all around the globe.

Biological Effects from Radiation

- Radiation Energy Level:** - the higher the energy levels (doses), the more the severe are the damages.
 - radiation doses are measured in *rads* (radiation absorbed doses – now an obsolete unit), 1 rad = 10 mJ.
 - *rems* (roentgen equivalent in man), 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)
- Penetrating Ability:** - the lighter the particles, the more penetrating they can be. In terms of penetrating ability: **γ ray is the strongest, followed by β particles and α particle is the least penetrating.**
- 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.



- 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
21.7 & 21.8 pg. 736 #50